

NUMBER ONE

THE WORLD WIDE CHEMICAL TRANSLATION SERIES

Edited by E. EMMET REID

Professor of Organic Chemistry, The Johns Hopkins University

NITROGLYCERINE AND NITROGLYCERINE EXPLOSIVES

BY

PHOKION NAOÚM, Ph.D.

*Director of Scientific Laboratories, Alfred Nobel
Dynamite Company, Hamburg, Germany*

AUTHORIZED ENGLISH TRANSLATION
WITH NOTES AND ADDITIONS

BY

E. M. SYMMES

*Hercules Powder Company
Wilmington, Delaware*

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PREFACE

This work in the important field of explosives is due to the plans of several experts to issue a large, comprehensive handbook of the entire technique of explosives. Difficulties encountered at the time did not allow this to be carried out, so that the author, to whom the preparation of the section on nitroglycerine and dynamite was entrusted, decided to issue his work as a special volume. This on one hand may explain the breadth of the treatment in including all matter worth while on the subject, and on the other hand, a certain limitation of material. For example, the theory of explosives in general is assumed to be known. A discussion of it seems unnecessary, particularly on account of the recent (1921) appearance of the classical work on explosives and detonators by Kast. It is also assumed that the ordinary methods of determining the value of explosives and blasting materials is known.

On the other hand, the technical side of the manufacture of nitroglycerine, with particular reference to recent advances and improvements, is treated at great length, as well as a careful characterization of nitroglycerine with critical consideration of previous publications, references to recent research and to experimental work by the author.

A special chapter is devoted to the nitric esters homologous with and related to nitroglycerine, wherein both the representatives of this group of theoretical interest as well as those explosive oils of commercial importance or in practical use or in the realm of possible commercial development receive their share of attention.

In Part III, dealing with the various nitroglycerine explosives, the author has not taken the trouble to give a complete picture of all existing mixtures and all proposals in the patent literature. The emphasis is rather placed upon the exposition of the present state of the art.

With an experience of twenty years and innumerable personal tests the author dares to hope that he has made a welcome contribution to the knowledge of an important branch of the art, which may be of use to all who manufacture, test or use explosives.

PHOKION NAOUM.

Schlebusch-Mannfort

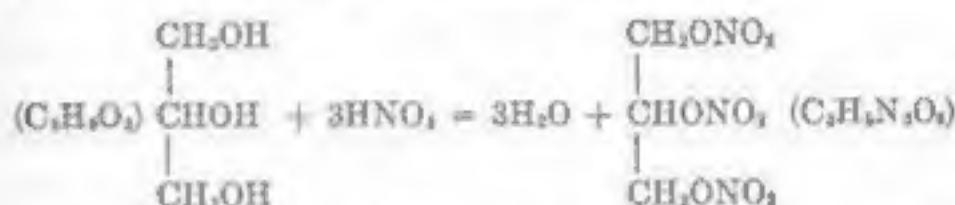
October, 1923

CHAPTER I

INTRODUCTION

Nitroglycerine, or Nobel's blasting oil, is really the trinitric ester of the trivalent alcohol, glycerine. Although the designation of nitroglycerine is incorrect, because the compound contains no nitro groups and therefore has no bond between the carbon and the nitrogen, it has been adopted and is the usual term, perhaps for the sake of brevity, until today it is retained in the art.

Nitroglycerine is formed by the combination of one molecule of glycerine with three molecules of nitric acid, splitting off three molecules of water, according to the following equation:



Under special conditions, such as when using certain acid concentrations, the glycerine may form the mono- and diesters, usually called mononitroglycerine and dinitroglycerine, which are always formed in small quantities of the manufacture of nitroglycerine. Each of these esters exists in two isomers, namely α - and β -glycerine mononitrate, and α , α - and α , β -glycerine dinitrate. While nitroglycerine is the basis of dynamite, and as such is the most important explosive in the art, mononitroglycerine is not an explosive, and dinitroglycerine, although a powerful explosive, has only been of temporary importance, and today is not manufactured.

DISCOVERY AND HISTORICAL REVIEW¹

Nitroglycerine was discovered in the early part of 1847 by Ascanio Sobrero (born 1812, died 1888), a pupil of the famous Pelouze, in Turin. He called it pyroglycerine, and described it before the Academy of Sciences in Turin in February 1847. The first printed

¹ See Guttman, *Die Industrie der Explosivstoffe* p. 17. Easales, *Nitroglycerine und Dynamit*, p.1.

reference is found in *L'Institut*, xv, 53, February 15, 1847. The section regarding the manufacture of nitroglycerine reads as follows:

M. Ascanio Sobrero, Professor of Industrial Chemistry at Turin, states in a letter communicated by M. Pelouze, that some time previously he had succeeded in producing explosive substances by the action of nitric acid on various organic substances, notably cane sugar, mannite, dextrine, milk sugar, etc.

M. Sobrero has also studied the action of nitric acid on glycerine. Experience has proved to him that a mixture of nitric acid and sulphuric acid is capable of giving a substance analogous to gun cotton. When a mixture of 2 vol. of 66° sulphuric acid and 1 vol. of 43° nitric acid is poured into syrupy glycerine, the reaction is very vigorous but it is one of oxidation. If the mixture of the two acids is kept in a refrigerating mixture and the glycerine added to it with stirring to hinder the elevation of the temperature, the glycerine dissolves without apparent action; if then the mixture is poured into water an oily material heavier than water is precipitated and collects at the bottom of the vessel. This can be washed with a large amount of water to rid it completely from the acids without loss since it is insoluble in this liquid.

Following this, the solubility of the oil in ether and alcohol, and its ease of precipitation from an alcoholic solution by water was mentioned, the color being given as yellow like olive oil.² It was said to have no odor, but a burning, aromatic taste. The readiness with which small quantities caused headache, the violent toxic properties, and its ability to detonate when heated were discovered.³

About 200 grams of the first nitroglycerine made by Sobrero is said to be still preserved in the Avigliana Nobel Dynamite Plant near Turin, where there is also a statue of the discoverer. This sample is tested annually. Although the explosive properties of this compound showed its value to the art, at that time the difficulties and danger in manufacture and use as an explosive appeared so great that the art took no notice of it and forgot it. It was used to a certain extent as a medicine in very dilute alcoholic solution under the name of glonoin.

It remained for the far-seeing spirit of discovery, the untiring energy and persistent activity shrinking from no difficulties and dangers, of the genial Swedish engineer, Alfred Nobel, almost twenty years after the discovery by Sobrero, to introduce nitro-

² Chemically pure nitroglycerine is colorless and as clear as water.

³ *Annalen der Chemie und Pharmazie*, 1848, vol. 64, p. 398, edited by Wöhler and Liebig, refers to the above article.

glycerine into the art with great success and to lay the foundation for its unexpected development. The story of nitroglycerine and dynamite made from it is closely connected with the tireless activity of Nobel. Overcoming great obstacles, he succeeded in perfecting the manufacture and use of the compound on a commercial scale, and in banishing as far as possible the dangers connected with both.

The conversion of the inconvenient and rather dangerous liquid nitroglycerine, which is difficult to handle, into a solid, either by absorption in porous materials like kieselguhr to form guhr dynamite or simply dynamite, or by formation of a colloid with nitrocellulose to form gelatine dynamite and blasting gelatine, as well as the certain and reliable detonation by adapting mercury fulminate percussion caps for use as detonating caps, were developments which even up to the present time have retained their importance, and are the results of the research activity of this man.

Alfred Nobel⁴ was born on October 21, 1833, in Stockholm, as the third son of a Swedish ship builder, Emanuel Nobel. His father, who among other things was engaged on the construction of land and submarine mines, was of an investigative turn of mind, particularly in the field of explosives. From 1859 on father and son busied themselves mainly with the study of explosives, and turned their attention particularly to the nitroglycerine discovered by Sobrero, the astounding properties and bright future of which, they well recognized. After Alfred Nobel had stirred up interest in his plans and had found the necessary means he erected at Heleneborg, near Stockholm, a small plant where nitroglycerine was made on a larger scale for the first time in 1862.

As a rule a pre-cooled mixture of strong sulphuric acid of a specific gravity of 1.83, and nitric acid of a specific gravity of 1.3, was used for nitrating, the glycerine being allowed to run into this. When using a stronger nitric acid, specific gravity 1.52, Nobel preferred to add the nitric acid in successive small portions in order to distribute the very appreciable heat of reaction, since at that time there was no commercial way of removing the heat because he nitrated in open jugs, and after each addition of glycerine the mixture was allowed to cool.⁵ The method given by Nobel for the preparation of concen-

⁴ For his family history and life see Escales, *Nitroglycerin und Dynamit*, p. 48.

⁵ Bavarian patent, September 1, 1866.

trated mixed acids by dissolving saltpeter in sulphuric acid and separating the acid sulphate was little used because of its inconvenience. Nitroglycerine then and for a long time thereafter was obtained by pouring the mixture after nitration into cold water, whereupon the heavy oil sank to the bottom while the acids were highly diluted and lost, in contrast to later improvements in the process, which gave a direct separation and recovery of the concentrated acids.

In the two years following Nobel's efforts were mainly directed toward the introduction of his explosive into blasting practice, and mainly to the most suitable manner of using the liquid nitroglycerine and means of reliably exploding it, and when things were beginning to look bright the young manufacturer met with a severe reverse in that his small plant at Heleneborg was completely destroyed by an explosion on September 3, 1864. This cost the life of Nobel's youngest brother, Oscar Emil, and the chemist Carl Erik Hertzmann, while his father, Emmanuel Nobel, was severely injured and suffered an apoplectic stroke from which he never recovered, dying in 1872. This accident, which made a deep impression upon the public, and which caused the government to forbid the manufacture of nitroglycerine in the vicinity of dwellings, did not discourage Alfred Nobel. In spite of all his misfortunes he held firm to his conviction that it would be possible by proper apparatus to overcome the innate dangers of the newest branch of the industry, and to place nitroglycerine, with its great advantages, in a proper place in the art. He rented a boat, anchored it in the Mälarsee, and continued with his experiments remote from dwellings. He soon found financial support in Hamburg, where "Alfred Nobel & Co.," the predecessor of the present great German explosive concern called the "Dynamit-Actien-Gesellschaft vormals Alfred Nobel & Co.," was founded. At the same time he built near Hamburg the first nitroglycerine and dynamite factory on the Continent, which supplied Nobel explosives to all countries in the world. At about the same time a factory was built at Vinterviken, near Stockholm, and then the use of nitroglycerine as an explosive spread through Germany and Sweden and export to other countries began.

The prospectus issued by Alfred Nobel & Co., Hamburg, in February, 1866, regarding the advantage of "blasting oil," is of great historical interest in the evolution of the art of blasting because it clearly set forth the great advantages over black powder, which for

centuries had been the only explosive, and its statements proved to have been absolutely correct and not exaggerated. All the advantages of the new explosive were even then properly recognized, in spite of the very primitive methods of use as compared to those of the present day, as well as certain defects in use which could not be eliminated all at once. The main points of that prospectus may therefore be given here, from the statements of Escales in his *Nitroglycerine und Dynamit*, page 18-20:

The following are the main advantages of "blasting oil:"

1. A large saving in drilling labor. The high specific gravity, the complete combustion and the extraordinary speed of the explosion of the patented "blasting oil" makes it the most powerful of all known explosives. The labor of drilling in all blasting is much more expensive than the explosive, consequently a saving in labor is more important than a saving in the explosive.

2. The possibility of completing the blasting in a shorter time.

3. The property of the "blasting oil" of not leaving any residue on explosion.

4. The high velocity of explosion, which is so high that the explosive action is not diminished by the presence of fissures in the rock, from which it is evident that merely loose sand or even water is sufficient tamping for "blasting oil." Since black powder burns much more slowly it is evident and has also been proved in practice that a borehole in fissured rock is much more effective with "blasting oil" than twenty to thirty boreholes loaded with black powder. For the same reason the patented "blasting oil" can also be used for blasting loose limestone, boulders, chalk, clay, wood, etc., where black powder is almost useless.

5. The safety in transportation and storage. The great danger with ordinary black powder of exploding from sparks, is not a factor with "blasting oil," but on the other hand it must be carefully protected from heat or violent shocks in a confined space.

6. The fact that boreholes can be loaded without any tamping, properly speaking. Since tamping of the boreholes need be only with loose sand or water, danger during loading is avoided, as well as time and money saved.

7. The saving in sharpening and tempering the drills. Since fewer boreholes are required with "blasting oil" than with black powder there will be a proportional saving in the cost of sharpening and tempering drills. When blasting in particularly tough rock this is a matter of no little importance.

8. The saving in fuse. The consumption of safety fuse is reduced in the same proportions, since fewer boreholes need be loaded with the "blasting oil" than with black powder.

9. Ease of loading wet holes. Since "blasting oil" is insoluble in water and because of its high specific gravity sinks rapidly to the bottom, wet holes can be loaded without "claying" or cartridging, merely by pouring the "blasting oil" into the borehole, whereas when using black powder "claying" is difficult and expensive.

10. The simple way in which submarine blasting can be done with it.

11. The possibility of blasting pieces of metal, etc. With "blasting oil" pieces of metal of all kinds, such as steel blocks, iron, old cannon, etc., of any size, can be broken up by using comparatively small boreholes and at low cost, which is impossible with black powder.

There then follow instructions and precautions for the use of "blasting oil."

The main difficulty was encountered in detonating nitroglycerine, since in contrast to black powder a direct spark or flame contact only caused it to burn slowly without detonating. Nobel therefore first used it as an addition to black powder and gun cotton, in order to raise the strength of the latter,⁶ exploding the black powder saturated with nitroglycerine by surrounding it with or superimposing upon it charges of black powder, or else he poured the "blasting oil" directly into the borehole and exploded it by cartridges of powder placed above it, or by patented detonators filled with powder. In horizontal or upwardly inclined boreholes he first loaded the nitroglycerine into sheet metal cylinders.

The devices he used in his attempts to make the use of nitroglycerine safe and convenient were various. The final result was only obtained by constructing a mercury fulminate percussion cap as a blasting cap, which involved the discovery of initiation, i.e., the production of detonation of an explosive not detonated by a flame by the wave of detonation of an explosive which does detonate by direct contact with a flame, which condition was at that time fulfilled by pure mercury fulminate, although by an appreciably larger quantity than when intended only for percussion caps for propellants.

While Nobel mentioned percussion caps in his 1864 patents and his patented detonators used black powder with mercury fulminate or finally mercury fulminate alone, the description of the mercury fulminate detonator is first found in his British patent 1345 of May 7, 1867, or Swedish patent of September 13, 1867.

Rudberg⁷ attempted to detonate nitroglycerine by means different from Nobel, namely by a sufficiently strong external shock, but naturally could not complete with the unfailing certainty of the Nobel initiation.

⁶ Swedish patent, October 14, 1863; British patent, 2350, September 24, 1863.

⁷ Swedish patent, May 31, 1865.

The knowledge that with the help of mercury fulminate as an initiator the detonation of nitroglycerine, gun cotton and many other compounds and mixtures whose internal combustion was accompanied by evolution of gases, could be readily initiated, first rendered the use of brisant explosives possible and disclosed the explosive nature of such compounds and mixtures.

This discovery was therefore a milestone in the development of the whole art.

The liquid form in which "blasting oil" was used in the first few years involved several dangers and disadvantages, aside from the very inconvenient form, and soon led to accidents in transportation and use. Leakage from the cans used to carry it and store it was a source of danger, on account of the sensitiveness of the oil to shock. Nitroglycerine which had run into fissures in the rock and failed to detonate caused explosions when picking out the broken rock.

At first Nobel tried to get around these dangers by dissolving the "blasting oil" in methanol so as to reduce the ease of detonation. At the point of consumption the nitroglycerine was separated out by shaking the solution with an excess of water and drawing it off. Mowbray in Massachusetts, made nitroglycerine at about the same time as Nobel, and carried it in a frozen condition in sheet metal cans to the mine, where it was presumably thawed in warm water. He had recognized the reduced sensitiveness of the frozen oil and utilized its tendency to freeze to reduce the danger in transportation. According to Guttman it was used for several years in this way in the construction of the Hoosac Tunnel in America. This rather inconvenient manipulation of the oil at the point of consumption, as well as the danger from the flammability of the solution, rendered these methods unsatisfactory, and Nobel then considered the question of giving the oil a more convenient and safe form. Chance led to the important discovery of the absorbency of infusorial earth. The sheet metal cans were packed in kieselguhr in order to protect them from shock and damage during transportation. The kieselguhr was obtained near the Krümmel factory, Hanover. When unpacking one of the cans it was found that one had apparently lost a portion of its oil, and in this way Nobel discovered the pronounced absorbency of kieselguhr for nitroglycerine, which was due to the capillary action of the minute diatomaceous particles of the kieselguhr. It was found that 25 parts of kieselguhr would convert 75 parts of the oil into a

cheesy plastic mass, hardly showing any exudation. This new mixture, which was more sensitive to shock than pure nitroglycerine, Nobel called dynamite, later guhr dynamite, to distinguish it from other mixtures.² This new form allowed the explosive to be packed into cartridges, which by exerting a gentle pressure on them would expand against the walls of the borehole and were so sure to handle and use that they were quickly adopted. Up to the middle of 1868 50,000 kg. of this new explosive had been sold. In an address Nobel gave the following statistics on the quantity of dynamite sold between 1867 and 1874: namely, 11, 78, 180, 324, 780, 1350, 2036 and 15,220 metric tons.

The discovery of absorption and absorption of the explosive, as by Kieselguhr to an astonishing degree, suggested the way for the new industry, so that Nobel could turn his energy toward forming everywhere companies and factories to use his patents. The next few years saw the following factories start: in Norway in 1866, California and Zanesville, Ohio in 1868, Hauge, Norway in 1870, Ardeer near Glasgow, Scotland, and Paris, France in 1871, Seefeldsch near Kitzbühel, Austria, near Bilbao, Spain in 1872, New York, Isenton, Switzerland, Augusta, near Lyons, France near Lisbon, and Pressburg, Hungary in 1873.

In spite of the difficulties which had been overcome, the introduction of dynamite was no easy task. It was largely a matter of overcoming the resistance of the makers, who with their conservatism fought against the use of the new explosive after they had used only black powder for centuries. Propaganda was also spread in favor of gun cotton.

Why he clung so closely to nitroglycerine was explained by Nobel in an address before the Society of Arts on May 21, 1875. He claimed that the concentration of power, velocity of explosion and safety are the three points upon which the success or failure of an explosive depends. Nitroglycerine, with its high density of 1.6, far exceeds gun cotton in energy density. It contains all the oxygen necessary for complete combustion of the carbon and hydrogen and even a slight excess of oxygen, while gun cotton, as a considerable oxygen deficiency, causing the formation of carbon monoxide on explosion.

² British patent 1345, May 7, 1867. Swedish patent September 9, 1867, Bavarian patent January 14, 1868.

Guhr dynamite still showed two defects. The nitroglycerine was readily detached from it by water, so that cartridges, as they dried before becoming wet and in wet boreholes there was the danger of nitroglycerine penetrating into fissures in the rock. For this reason the ordinary paper wrappers were unsuitable for use in water. Furthermore it contained 27 per cent of inert material which was not converted into gases but which on explosion absorbed energy by breaking down into dust and absorbing heat. This is one of the main reasons why the first test in the Trazz with 10 grams of guhr dynamite does not give a value 75 per cent of the expansion given by 10 grams of high nitroglycerine, but only considerably less. Ten grams of nitroglycerine gives about 80 cc., 75 per cent of which is 45 cc., while 10 grams of guhr dynamite gave only about 32 cc.

Many attempts were then made to replace the guhr by other suitable absorbents, only those which would be converted into gases, to replace the inactive inert material. Among these considered were charcoal impregnated with sulfur to prevent its burning, wood meal, refined wood meal, addition of sugar, starch or gelatin, and pulped gun cotton. While in some countries such as the United States, Austria and France cartridges with a guhr base continued for a long time, and in America for example explosives composed of liquid nitroglycerine and absorbents are made even today. Also with a high nitroglycerine content suffered from the disadvantage of not retaining the solid form, etc., and were soon superseded on account of a new, epoch-making discovery of Nobel.

Chance, a scull winder, is said to have drawn his attention to colored solutions of solutions of low nitrogen nitrocellulose in ether alcohol. By allowing a mixture of nitroglycerine and this solution to evaporate he obtained a gummy, plastic mass, which he also obtained by mixing directly 7 to 8 parts of emulsion nitrocellulose with 93 to 92 parts of nitroglycerine. The emulsion nitrocellulose first dissolves to a thick liquid which on warming up to 60 to 70°C. in fifteen to twenty minutes or at ordinary temperatures in a few hours, forms a solid colloid, a tough plastic elastic transparent gelatin of a light brown color, the so-called blasting gelatine, which combines all the ideal properties of a highly brisant explosive, namely conversion into the gases carbon dioxide, nitrogen and water vapor, without leaving a residue of high density and absolute insensitiveness to moisture, thus rendering it suitable for blasting under water.

The excess of oxygen of the nitroglycerine just about suffices to equalize the oxygen deficiency of the nitrocellulose.

Here we have an explosive of the very highest energy content and greatest energy concentration, which was called into service in blasting the very hardest rock with satisfaction, namely in the construction of the Gotthard tunnels, and which forms the basis of the gelatinous explosives which rapidly came into use to the widest extent because of their characteristic properties, high density, insensitiveness to moisture, and high effectiveness as compared to the old guhr dynamite, which they far surpassed.

By reducing the quantity of carbon nitrocellulose there is obtained a thinner sort of gelatine which is not sufficiently firm to be used as an explosive by itself, but which can be incorporated readily with wood meal and saltpetre to form a paste mass, and which is then an active base dynamite simply retaining the nitroglycerine and not even giving it up when water is added. Nobel called these mixtures gelatine cylinders. In certain respects gelatine cylinders represent a weakened blasting gelatine. It is less brisant and cheaper. The following composition is typical and is the most widely used: nitroglycerine 62 per cent, carbon nitrocellulose 20 per cent, wood meal 8 per cent, sodium nitrate 27 per cent.

This new discovery was patented by Nobel, and this comprises in all countries. The German patent describes a process for the preparation of an explosive from nitroglycerine and carbon nitrocellulose with the addition of means to increase or decrease the explosive effect. In this description he says:

On mixing the gelatine there is obtained a compound, or solid gelatine, depending upon the nitrocellulose content, and by the addition of blasting gelatine in the cartridges are prepared with a blasting further material, or with the admixture of materials which

partly increase the explosive effect of the preparation and is safe against rifle shots, such as metallic carbide, are also a time absorber, or benzene, camphor, etc.,

partly, as a means of obtaining of decomposition products, for example, gas carriers, like sodium nitrate, potassium nitrate, etc.

or partly change the brisant effect of the explosive, for example, soot, shattering like black powder, etc.

These cartridges considerably surpass the cartridges consisting of carbon glycerine powder, and are sufficiently strong and safe.

* German patent 4829, February 18, 1875, or, 1876 patent 4, 10 December 2, 1876.

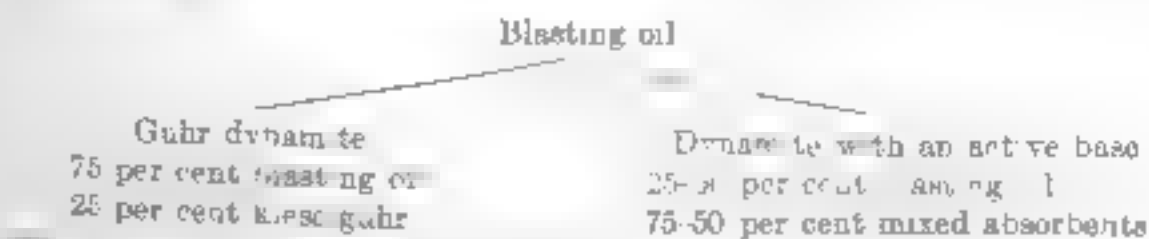
The patent claim reads:

The process of converting nitroglycerine, or methyl- or ethyl nitrate into a solid form by gelatinizing with low-nitrogen cotton and rendering the mass less dangerous by adding substances.

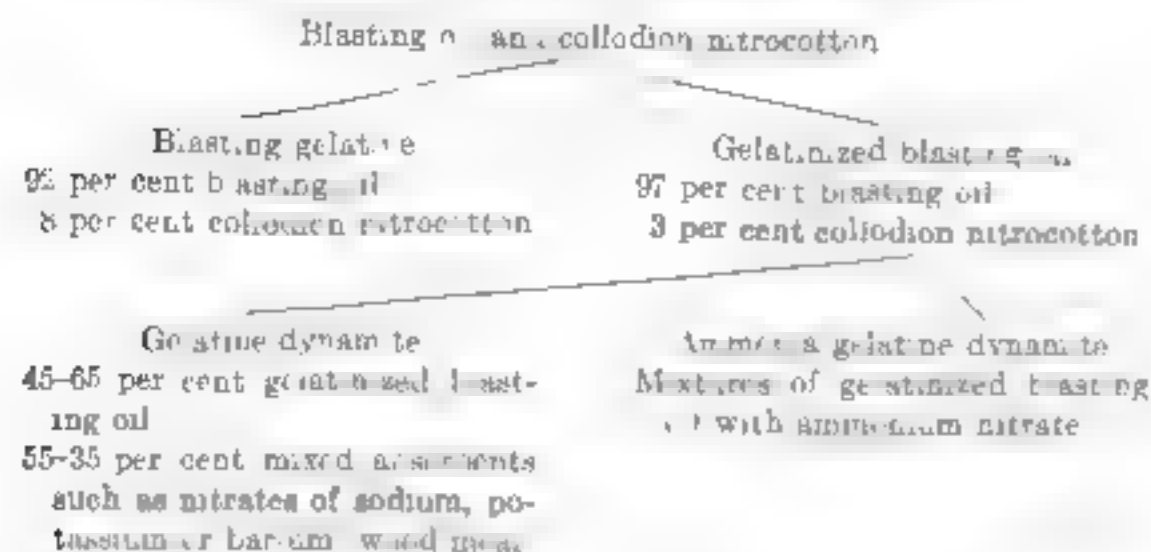
Attempts were made in Austria by Sarsch, a chemist, and Captain Hess, to make blasting gelatine suitable for military purposes. By incorporating camphor it was possible to make blasting gelatine relatively safe to handle.¹⁰ Such a camphorated blasting gelatine was used for a long time by various armies. The Russian army even used it in the World War. However, nitroglycerine explosives as munitions achieved little importance on account of their relatively dangerous nature, particularly if struck by a bullet.

At about the same time Nobel added ammonium nitrate to his nitroglycerine explosives, and on July 22, 1879, took out a Swedish patent for extradynamite, ammonium-guhr dynamite, which was a fortified gelatine dynamite of the following composition: nitroglycerine 71 per cent, nitrocellulose 1 per cent, charcoal 2 per cent, ammonium nitrate 23 per cent. In the same patent there was given a composition low in nitroglycerine, namely, nitroglycerine 20 per cent, nitrocellulose 1 per cent, charcoal 2 per cent, ammonium nitrate 62 per cent, which referred to an explosive not gelatinous but granular plastic, and of which makes it evident that Nobel clearly recognized the significance of ammonium nitrate in the explosive industry. The basic type of the later safety ammonium nitrate explosives had already been claimed by the two Swedes, Ollsen and Norrbin, who in 1867 patented under the name of ammoniakkrut a mixture of ammonium nitrate and charcoal or other carbonaceous material. Nobel, recognizing the future of the idea, bought the rights from his countrymen.

The following diagrammatic scheme of the course of the development of nitroglycerine explosives up to this time is taken from *Nitroglycerin und Dynamit* by Esenke:



¹⁰ German patent 5025, July 2, 1876.



Although as previously mentioned nitroglycerine played only a minor rôle as the basis of highly brisant explosives for military purposes, it attained an unexpected importance in munitions as a result of the last great discovery of Nobel namely smokeless nitroglycerine powder first called Balistit, and which caused a complete revolution in propellant powders. In the World War nitroglycerine was the most indispensable component of munitions. By far the greater proportion of the war is production of glycerine was converted during the war to smokeless powder plants. Starting with blasting gelatine Nobel succeeded by increasing the nitrocellulose content in producing a firm, brownish yellow which no longer detonated by a blasting cap but proved to be a very stable, powerful propellant, on account of its slow combustion.

Long and fundamental research finally evolved Balistit a mixture of 40 per cent nitroglycerine and 60 per cent collodion nitrocotton the latter in part gun cotton, which was patented in 1888.¹² About a year later Abet and Dewar members of the English Explosives Commission, patented a smokeless powder made up of nitroglycerine and nitrocellulose by a similar process which was used in the English army under the name of Cordite and which contained still more nitroglycerine than Balistit.¹³

These astounding discoveries for that period, namely that two of the most brisant and sensitive explosives, when brought into certain definite proportions and in a certain physical condition, gave a propel-

¹² British patent 1491 January 3, 1888, German patent 5147, July 3, 1889.

¹³ British patent 5614, April 2, 1889, British patent 11664, July 22, 1889.

lant no longer explosive but slow burning, were Nobel's last efforts and to a certain extent the conclusion of his work. The enormous application of these two inventions twenty-five years later in the World War he the founder of the Peace prize hardly foresaw and certainly did not desire. After residing for eighteen years in Paris he moved to San Remo in 1891, where he died on December 10, 1896 but to the last with research and new problems. The legacy, known all over the world, left by this man testifies to his high character not only as a skilful research worker and active manufacturer but one who advanced civilization.

The composition of the principle types of brisant nitroglycerine explosives of Nobel has not been changed up to the present time. Their efficiencies and properties have not been surpassed in almost a half century by any new discoveries although for certain purposes they have had competition in the form of safety ammonium nitrate explosives and the less safe chlorate and perchlorate explosives to which must be added in recent times the very effective mixture of liquid oxygen and carbonaceous materials. The latter adaptation of the latter in Germany was the result of the blockade during the World War and the consequent scarcity of raw materials for the manufacture of explosives.

Soon after Nobel's discoveries there early recognized requirements of mining made a reduction in the brisant properties of dynamite, and a reduction in its temperature of explosion, velocity of detonation and pressure of explosion necessary. Attempts were made to produce explosives which on firing in coal or in adjacent rock would not ignite mixtures of fire-damp or coal dust and air, as was the case with even small charges of black powder and dynamite. This was called making them safe in fire-damp or coal dust. Government Mine Gas Commissions were appointed in France in 1877, in England and Belgium in 1879 and in Germany in 1880 investigated the conditions practically and theoretically and set up standards for the safety in fire-damp of explosives which were based upon the results of their research.

While it was found in the course of time that every type of explosive could be made safe in fire-damp and coal dust by the addition of certain and avoidance of other components, the nitroglycerine explosives were for a long time the most important as the basis of safety explosives for mining purposes. However, the World War

taught us how to make even the chlorate and perchlorate explosives permissible. Nobel Extra Dynamit Type II, a mixture of 70 to 80 per cent ammonium nitrate and 30 to 20 per cent gelatinized nitroglycerine, was the first representative of this class. In France and Belgium a similar one called Grisoutine was used.

The real pioneer work in this field was done in Germany by E. Müller, General Director of the Rheinisch-Westfälische Sprengstoff-A.-G. and G. Autschlager, General Director of the Dynamit-A.-G. vorm. Alfred Nobel & Co. who made the best type of the German "Wetter-Dynamit" by adding to dynamite considerable amounts of salts containing water of crystallization, such as soda crystals, alum, magnesium sulphate, borates, phosphates in order to cool the gases of explosion by evaporation of the water of crystallization and so reduce the temperature of explosion.¹ Further development of this new class of explosives was done by the Sprengstoff-A.-G. Carbenit, founded by Carl Bauer, which also marketed Carbonites of the desired type in 1887. They contained 25 to 30 per cent liquid nitroglycerine, 25 to 40 per cent meal and the rest potassium or sodium nitrate. Some time later paste or gelatinous explosives of this type were made by gelatinizing the nitroglycerine with collodion nitrocotton. This produced the Gelatin Carbonites, Nobelites and permissible gelatin dynamites with 25 to 40 per cent gelatinized nitroglycerine. Ammonium nitrate and common salt thereafter played an important part in the composition of these explosives. Fundamental research by B. v. Lang, Chief of the Bergwerkschaftliche Versuchsstrecke at Gelsenkirchen led in 1888-1909 to a tightening of the requirements for permissibility of explosives and in connection therewith to a further reduction in brisance. Chapter 5 of Section 3 gives further details. A similar elaboration of the requirements soon appeared in England. Even today gelatinous nitroglycerine explosives play an important part in coal mining and are in considerable demand.

A certain popularity was enjoyed in the last decade by a special type, furnished by the Carbenitfabrik Schleierbach, which may be considered as both an ammonium nitrate and a nitroglycerine type containing about 12 per cent nitroglycerine with a rather small addition of nitrocellulose. Gelatine Carbonit C. Neu-Nobel. It differs from the true ammonium nitrate explosives in having a higher

density and less safety in handling, and from the Nobelites in its non-gelatinous nature.

After this description of the course of the development of dynamite and similar explosives, which always remained dangerous to handle with all their improvements and reductions in strength as for example for coal mining explosives and which could therefore only be shipped under certain conditions, the important part which nitroglycerine has played for a long time when present in small quantities in safety ammonium nitrate explosive should not be forgotten. An addition of only 4 per cent of nitroglycerine has been adopted for the ammonium nitrate explosives first for those used in rock and then for the permissible type. The first of these explosives was Donant brought out by the Carbenitfabrik, consisting of ammonium nitrate, trinitrotoluene, cereal meal and 4 per cent nitroglycerine followed by Astralit of similar composition brought out by the Dynamitfabrik Schleierbach. The addition of nitroglycerine slightly raised the density of these powdery mixtures and improved the ease of detonation to a considerable extent as well as the propagation and velocity of detonation. On the other hand the small quantity of finely dispersed nitroglycerine did not affect unfavorably the safety in handling so that such explosives were permitted on German railroads as ordinary freight without restriction.

In concluding this historical review there might be mentioned briefly the efforts which have been made to avoid one of the main disadvantages of nitroglycerine and explosives made from it, namely, the readiness with which it freezes. These efforts were innumerable and are as old as the use of nitroglycerine. The solution of the problem of rendering nitroglycerine non-freezing was only attained about the middle of the first decade of this century and although this solution, contrary to the opinion of many, was perfect from a technical point of view, at least for the winter climate of Europe, perhaps justified to some extent for the far North. It is worth noting that only relatively little use of this important practical development was made thereafter in Germany. The new compounds added raised the manufacturing cost of the product and the producers were forced to raise the selling price slightly, whereupon many customers found that they preferred to thaw frozen dynamite in hot water thawing kettles, just as they had done before, instead of paying the small increase in price in spite of the fact that previously they

¹ British patent 12424, 1887, French patent 185809, 1887.

had repeatedly demanded non-freezing explosives. The reason for the small use of these non-freezing explosives was therefore commercial and not technical. The thawing seemed to the customer more advantageous, and the inconvenience, of which he had previously made so much, was then considered unimportant. Thus the results of a practical improvement, the development of which had required inventive genius, ingenuity and much painstaking work, were wrecked by a small financial perfection. In spite of this the problem which had engaged Nobel and subsequently many chemists is today solved and there are available non-freezing dynamites which are in no way inferior to those containing the nearly freezing nitroglycerine.¹⁴

Nitroglycerine freezes at $+13^{\circ}\text{C}$. Its velocity of crystallization is indeed rather slow, particularly when in the form of a gelatinous explosive, but on long storage in cold weather all preparations containing nitroglycerine freeze to a mass as hard as stone, which thaws slowly, and which is unsuited for an excessive amount of pressure and insensitiveness. Although theoretical considerations and laboratory experiments show the low sensitiveness and safety of detoning the frozen as compared to the liquid nitroglycerine, accident statistics show the opposite. An English compilation of accidents for example, shows 87 per cent of all accidents with nitroglycerine explosives to have occurred in the cold part of the year.¹⁵ The main causes of this peculiarity may be due to the use of unsuitable methods of thawing and particularly to careless handling of frozen dynamite. It is possible that on thawing some of the liquid nitroglycerine escaped from the cartridges and increased the risk in handling them.

The first attempt to reduce the freezing point of nitroglycerine was made by Radberg, by adding other materials like benzene or nitrobenzene.¹⁶ Later Nobel made similar attempts, and proposed the addition of methyl and ethyl nitrate, nitrobenzene or acetone.¹⁷ Others proposed to add or ho nitrobenzene, amyl nitrate and isobutyl

¹⁴ Today non-freezing explosives are used mainly in the United States, Canada and Scandinavia. TRANS. AM. CHEM. SOC.

¹⁵ Decker, *Umfassende Statistik von Sprengstoffen*, Internationaler Kongress, 1903, Sektion 3b, Vortrag.

¹⁶ Swedish patent, April 30, 1866.

¹⁷ Swedish patent, July 8, 1876.

nitrate. While methyl and ethyl nitrates were suitable from a chemical point of view, their volatility hindered their use. The other compounds proposed were not effective in small quantities. When added in large quantities, so as to appreciably reduce the freezing point of the nitroglycerine, they desensitized the latter to such an extent that sensitiveness and brisance were too much reduced.

An indication of how the difficulty might be overcome was given by Wobl in his German patent 58347, August 17, 1890, who polymerized glycerine and then nitrated the product. This made an explosive oil which we immediately recognize as difficult to freeze, but the process attracted no attention at that time.

Sigurd Naessloff investigated the question of reducing the freezing point of nitroglycerine in a thoroughly scientific manner, explaining it clearly, and showed that all previously proposed agents could not completely achieve their purpose and why. However, his investigations gave no indication of the proper manner of obtaining this goal.¹⁸ He found as was to be expected, that every material dissolved in nitroglycerine caused a lowering of the freezing point of the latter, but a property proportional to the concentration and inversely proportional to the molecular weight of the dissolved substance, provided that the dissolved material neither associated nor formed complex molecules. His substances proposed by Naessloff for additions to lower the freezing point met fairly favorable conditions: (1) solubility in nitroglycerine; (2) lowest possible reduction in explosive power; (3) low volatility; (4) no unfavorable effect upon the gelatinizing power of nitroglycerine; (5) no unfavorable effect upon the chemical stability of the explosive, which shows why the addition of nitrobenzene or ethyl nitrate did not accomplish its purpose.

At times plastic and low-freezing explosives similar to dynamite were made by adding nitrobenzene and nitrotoluene, the explosive oil consisting of about 75 per cent nitroglycerine and 30 per cent mono-nitro compounds. However, such mixtures must contain less explosive oil and more saltpeter because of the high oxygen deficiency of the nitrocompounds, and for various reasons they cannot be satisfactory substitutes for high strength dynamites.

The solution of the problem was more closely approached by the

¹⁸ *Z. angew. Chem.*, 1891, 44, pp. 11 and 53.

use of the highly nitrated aromatic hydrocarbons, especially the low-melting, eutectic mixtures of the isomers of di- and trinitro-durene, which dissolve readily in nitroglycerine even at low temperatures and desensitize it very slightly, less than the mono-nitro-compounds. However, even by the use of these absolutely non-freezing and high strength dynamites could not be made which were satisfactory in all respects.

Meanwhile Dr. Anton Maazajczak in his patent application of August 5, 1903, on the preparation of dynamite pointed out the right way, which from that time on was followed eagerly by several explosive plants. In his remarks of 1904 (page 6) on "New explosives" he spoke of dinitroverine as an explosive and mentioned its property of reducing the freezing point of nitroglycerine. The possibility of making the mixture sturdier was known previously, but the literature contained no exact directions for its preparation and only dubious statements as to its properties. Maazajczak was the first to give a simple method of producing nitroglycerine in good yields and free from trinitroverine and a close study by others¹⁹ soon cleared up the matter. Intensive research in this field now showed that nitro esters belonging to or related to nitroglycerine, such as dinitroverine, dinitrochlorohydrine, tetranitroverine, tetranitroglycerine or the nitrate of polymerized glycerine or nitroglycol, due to their property of mixing with nitroglycerine in all proportions and their equivalent explosive strength were suitable in proper proportions for the manufacture of low-freezing explosives and dynamites. These esters crystallize with far more difficulty and at lower temperatures than nitroglycerine, and in spite of their high molecular weight, which according to the above-mentioned law would render them less suitable, they give with nitroglycerine eutectic mixtures of very low freezing points, practically unfreezable because of the low velocity of crystallization. Even when the quantity added to nitroglycerine is insufficient to cause absolute impossibility of freezing, they have very marked on raising the temperature, in contrast to nitroglycerine. Apparently the degree of chemical relationship plays an important part in the crystallizing point of the so-called eutectic mixtures, in addition to the law of molecular lowering of the freezing point.

For example, a mixture of 25 to 30 parts of dinitroverine and

¹⁹ German patents 181385 and 181561

75 to 70 parts of nitroglycerine is difficult to freeze, and a 40 to 60 mixture practically impossible to freeze. Likewise a mixture of 30 parts dinitrochlorohydrine or nitroglycol and 70 parts nitroglycerine is practically unfreezable. What is true of the oils is also true of the explosives made from them. Since each of the esters is a powerful explosive in itself, their mixtures with nitroglycerine in the proportions of about 30 to 70 can hardly be differentiated from that of pure nitroglycerine as regards explosive strength.

While dinitroverine, the discovery of which gave rise to these other inventions, came into very little practical use on account of its solubility in water, requiring a rather inconvenient method of manufacture, and was used only by the Sprengstoff-Gesellschaft (Astrop in Westphalia and later by the Westfälische Sprengstoffwerke at the Rumbach plant in Westphalia for some years for the manufacture of low-freezing dynamites and peroxide explosives, dinitrochlorohydrine, whose use was patented by the Dynamit-Aktion-Gesellschaft vorm. Nobel & Co., is still used today to make non-freezing dynamites, especially as a base, see introductory remarks in this connection. Dinitrochlorohydrine is obtained by nitrating monochlorohydrine, which was formerly an expensive compound. After its commercial importance was recognized, processes for making it were soon discovered. Tetranitroglycerine, the manufacture of which was patented by the Zentralstelle für wissenschaftlich-technische Untersuchungen at Neuwaldeberg, Potsdam, has up to the present time found little use in Germany on account of certain technical difficulties in manufacture²⁰ which dinitrochlorohydrine does not present. Further data on these questions, together with patents and literature citations, will be found in the chapters on Nitroglycerine Homologues and Non-Freezing Dynamites.

Nitroglycol, or glycol dinitrate, which assumed a prominent position among the above compounds as regards its explosive power, did not at this time come into use on account of the difficult synthesis of the raw material, ethylene glycol, although, the material had been patented in 1904²¹ as a material to reduce the freezing point of nitroglycerine.²²

²⁰ It has been widely used in the United States since about 1912.
TRANSLATOR.

²¹ German patent 174879

²² It is now offered and sold in large quantities in the United States. — TRANSLATOR.

The World War, with its confiscation of glycerine for military purposes, turned attention in Germany to it as the only completely satisfactory substitute for nitroglycerine, perhaps even a true competitor.

The fact that glycerine is produced cheaply in large quantities from cheap natural products, largely as a commercial by-product, seemed to prevent any competition of chemically similar explosives taking into consideration the almost ideal explosive formula of nitroglycerine. As a matter of fact, there are only two other liquid nitrate esters which equal its favorable explosion formula, namely methyl nitrate and nitroglycol. While the former cannot be seriously considered on account of its low boiling point, 65°C., and its high volatility, nitroglycol, with its ideal formula decomposing smoothly on explosion to carbon dioxide, water and nitrogen according to the equation $(C_2H_5NO_2)_{12} = 24CO_2 + 24H_2O + 3N_2$, is an ideal explosive oil, but it has been given little consideration on account of the high price and difficult synthesis of its raw material, glycol, which latter does not occur naturally in large quantities as contrasted to the advantage of the cheap triglyceride. The enormous requirements of the latter during the war, and the ensuing lack of fats caused by the blockade of the Central Powers, caused a search for substitutes, and attempts were then made to carry out the synthesis of glycol and make it a commercial process. The Gesellschaft A.G., of Essen built a large plant in which they produced glycol in considerable quantities from alcohol via ethylene and ethylene chloride, the latter being saponified in an autoclave. They put it out as an article of commerce. Although nitroglycol could not be used in the manufacture of smokeless powders on account of its volatility, higher than that of nitroglycerine at moderate temperatures, it formed a complete substitute for nitroglycerine in gelatinous mining explosives, and many tons of it were produced during the latter years of the war in the domestic explosive plants. When the large stocks of glycerine were released after the war for mining purposes the production of glycol, which had been limited by the scarcity of alcohol and chlorine, again ceased. With abundant and cheap glycerine, nitroglycol was pushed into the background unless a discovery of a very cheap source of ethylene, independent of alcohol,²² and a lower price of chlorine again alters the picture.

²² For example from natural gas. TRANSLATOR

It should be added here that the value of nitroglycol, which is slightly greater than nitroglycerine in brisance and velocity of detonation, should be increased by its high degree of safety in handling. In recent times the Dynamit Actien Gesellschaft has succeeded in making absolutely safe gelatinous explosives on the basis of gelatinized nitroglycol and ammonium nitrate, which are allowed on railroads as ordinary freight without restriction under the name of Gelatin-Astrait, which are in no way inferior to gelatine dynamites in explosive strength and which have the additional advantage of being non-freezing.

After this historical review of the discovery and introduction of nitroglycerine into the technique, as well as its use in various explosives, there remains only a word to be said about the development of the manufacturing process itself. However, since a description of its manufacture by various methods and their improvements will be found at the proper place in this book, only the main steps of the development will be given here, in order to avoid repetition.

Originally a large number of small glass or porcelain vessels were used for the reaction, with primitive agitation by hand. This very gradually grew into the use of glass reaction vessels, and finally into the present extensive use of large cylindrical lead vessels. With the increasing size of the charges mechanical stirring followed hand agitation, and in turn compressed air, completely displaced the former.²³ Compressed air agitation was used by Mowbray in the United States in the sixties. Somewhat later, about 1877, it became possible to separate the acid directly from the concentrated acids and recover the latter, which was an important economical and technical improvement. Before previous to this time the nitroglycerine had been separated by drawing the entire charge in a large volume of water with complete loss of the spent acids. The French Boutmy and Faucher nitrating process of removing the heat of reaction to reduce the danger of decomposition by first mixing glycerine with sulphuric acid and then mixing this with the nitric-sulphuric acids involved such difficulties as to overbalance the over-estimated advantages. It was used only at a few places and in time was dropped.

An important economical improvement in manufacturing proc-

²³ Except in the United States where mechanical agitation is universal. TRANSLATOR

esses toward the end of the century was the conversion of the large German and English factories to the manufacture of fuming sulphuric acid and consequently an enormous saving in nitrating acids when upon the nitroglycerine yield rose about 10 to 15 per cent, or from about 20-25 to 225 parts per 100 parts of glycerine used. About ten years later some of the same factories raised the yield to 230 per cent by using artificial refrigeration or cooling by brine at 12°, so that nitrating temperatures could be reduced from 25-30 to 12-15°C.

A rather important gain in the capacity of the plant and an increase in safety were brought about when small additions of paraffine oil, vaseline or sodium stearate, sometimes mixed with kerosene, were used in the charge to reduce the time of separation of the nitroglycerine from the spent acids.²

² German patent 7,108, May 21, 1904, 48489 October 2, 1905 and 28,661 October 1, 1906.

PART I

NITROGLYCERINE

CHAPTER II

METHODS OF PREPARATION

Nitroglycerine is formed by the action of nitric acid on glycerine. The formation of one molecule of nitroglycerine requires one molecule of glycerine and three molecules of nitric acid, setting free three molecules of water, or expressed in gram-molecules, 92 grams glycerine + 189 grams nitric acid = 227 grams nitroglycerine + 54 grams water.

One hundred parts of glycerine thus give theoretically 246.7 parts of nitroglycerine, requiring 205.4 parts of nitric acid and setting free 58.7 parts of water. However, if glycerine is added to such a calculated quantity of practically anhydrous nitric acid the formation of nitroglycerine soon ceases, and the nitric acid, diluted by the water formed, soon starts a process of oxidation. For complete conversion of glycerine into glycerine trinitrate it is necessary to have not only an excess of nitric acid molecules but also a dehydrating agent which will maintain a sufficient concentration of the esterifying nitric acid. Although for the reasons set forth below only sulphuric acid is of importance commercially for this purpose, on purely theoretical grounds any dehydrating agent is suitable which reacts neither with glycerine nor with nitric acid, or which only forms compounds with glycerine which break up with the excess of nitric acid, such as sulphuric acid, which forms temporary glycerine sulphate, broken up by suitable concentrations of nitric acid.

The first dehydrating agent considered was nitric acid itself. The following tests, which are of purely theoretical interest, illustrate the possibility of converting glycerine almost completely into nitroglycerine, without the use of sulphuric acid:

1. *With nitric acid alone.* An appropriate excess of nitric acid converts glycerine almost completely to nitroglycerine.

Example: 100 grams of glycerine were put into 1000 grams of 99 per cent nitric acid, whereupon considerable heat was developed, which was removed by cooling with ice water. It was allowed to stand in ice water for an hour to permit the reaction, whose velocity falls with dilution of the nitric acid, to come to an equilibrium, and then poured into three liters of ice water, whereupon the

greater portion of the nitroglycerine separated as an oil. Washing and neutralization gave 176.5 grams of oil. The dilute acid was then shaken with chloroform. After separating and neutralizing the chloroform solution by a solution of sodium carbonate, and distilling off the chloroform 30.7 grams more oil were obtained, or a total of 207.2 grams or 207.2 per cent of nitroglycerine, based upon the glycerine used, corresponding to 84 per cent of theory. The nitroglycerine contained 18.16 per cent nitrogen, the theoretical being 18.50 per cent, so that it contained some glycerine dinitrate. If less nitric acid had been taken, for example five times the quantity of glycerine, a mixture of glycerine trinitrate and dinitrate would have been obtained.

Such a process must naturally be uneconomical because the large excess of costly nitric acid is only recovered in a very dilute form, or after neutralization and evaporation as sodium nitrate.

2. *With nitric acid and phosphorous pentoxide.* A mixture of 400 grams of the strongest nitric acid and 150 grams of phosphorous pentoxide is made while cooling well, and while still cooling down 100 grams of glycerine added to the thick liquid, whereupon the phosphoric acid falls to the bottom as a thick syrup and the nitroglycerine formed remains dissolved in the strong nitric acid. By separating the thin layer from the syrup and precipitating by adding ice water about 200 grams of pure nitroglycerine were obtained. If 100 grams of glycerine are first dissolved in 400 grams of nitric acid and while cooling with ice water and vigorously stirring 150 grams of phosphorous pentoxide added in small portions at a time the solution can likewise be readily separated from the phosphoric acid syrup and the nitroglycerine obtained by precipitating the solution with ice water. After thorough purification the yield is about 200 per cent.

3. *With nitric acid and anhydrous calcium nitrate.* One hundred grams of glycerine are dissolved with cooling in 500 grams of the strongest nitric acid, and 400 grams of powdered, absolutely anhydrous calcium nitrate added. There is only a slight development of heat. After standing for several hours the thin broth is added to several times its volume of cold water, which gives about 220 grams of nitroglycerine containing about 10 per cent dinitroglycerine, corresponding to about 200 grams of nitroglycerine. By merely dissolving 100 grams of glycerine in 500 grams of nitric acid there is obtained only about 50 grams of nitroglycerine and 140 grams of dinitroglycerine (which see).

Only concentrated sulphuric acid, the strongest, cheapest and most convenient dehydrating agent comes into consideration in the commercial manufacture of nitroglycerine, because its use makes it possible, with a comparatively slight excess of expensive nitric acid, to obtain nitroglycerine in high yields and almost completely free from glycerine of lower degrees of nitration, and at the same time to separate the oil directly from the concentrated mixture of spent acids and recover the latter in a valuable form for re-use. While 10 parts of the much less energetic dehydrating agent, concentrated

nitric acid, are required to completely convert 1 part of glycerine into nitroglycerine, a mixture of $4\frac{1}{2}$ parts of concentrated sulphuric acid and about 3 parts of 90 per cent nitric acid produces about 2.15 parts of pure nitroglycerine from 1 part of glycerine. By using fuming sulphuric acid (oleum) containing 20 per cent free SO_3 a mixture of 360 parts with 280 parts of 90 per cent nitric acid is sufficient to produce about 225 parts of nitroglycerine from 100 parts of glycerine.

Of the three possibilities: (1) solution of glycerine in nitric acid and complete esterification and separation of the nitroglycerine by a subsequent addition of sulphuric acid, (2) solution of glycerine in sulphuric acid and mixing this with nitric acid and sulphuric acid (Boutmy-Faucher process), (3) gradual addition of glycerine with constant cooling to a nitric-sulphuric acid mixture, with almost complete separation of the nitroglycerine, only the third can be considered as a commercial method. While for various reasons the first would be disadvantageous from a tendency of the glycerine, dissolved in a small quantity of nitric acid, to oxidize and to heat up strongly when adding sulphuric acid, the second method, which separates the heat formation into two portions and consequently reduces its intensity in practice, did not endure, so that only the third method remains. It was the original method used and is to-day the only one by which nitroglycerine is made.

PREPARATION OF SMALL QUANTITIES OF NITROGLYCERINE IN THE LABORATORY

To prepare small quantities of nitroglycerine in the laboratory as simply as possible the following method is used:

Six hundred and thirty grams of nitrating acid are weighed into a cylindrical lead vessel holding about a liter, and having an outlet cock. This acid should contain 39 to 40 per cent HNO_3 , 59 to 60 per cent H_2SO_4 and as little water as possible, and can be made by slowly adding 350 grams of fuming sulphuric acid containing 20 to 25 per cent free SO_3 to 280 grams of at least 90 per cent nitric acid, while cooling and stirring. If fuming sulphuric acid is not available, the quantity and composition of the nitrating acid is changed, for example, 300 grams of the above nitric acid are mixed with 450 grams of 66° (98 per cent) sulphuric acid, forming a nitrating acid of about 36 per cent HNO_3 , 59 per cent H_2SO_4 and

5 per cent H_2O , which will give a somewhat lower nitroglycerine yield. The lead jug is placed in a lead vessel provided with an inlet and outlet for water, so that it can be cooled by running water. The lead jug is preferred to a glass beaker on account of the more rapid cooling due to better heat conduction and the fragile nature of the glass. The glycerine, 100 grams of dynamite glycerine as free from water as possible and of 31° Bé or 1.26 specific gravity, is warmed to 40 to $50^\circ C$. to render it more fluid, and allowed to drip from a dropping funnel to a point between the center and the rim of the lead jug after the acids have come to the temperature of the cooling water, while being vigorously stirred by a thermometer, which is read after each addition of glycerine. This precaution is necessary because the dropping glycerine must be immediately distributed into a large quantity of acid in order to avoid local overheating and oxidation, which would cause a violent, or under certain conditions dangerous, decomposition of the charge. To avoid local decomposition, which is accompanied by a slight bubbling or development of red vapors, the agitation must be quiet and regular, and drops of glycerine on the walls of the jug avoided, since they can be oxidized by small amounts of the acid and give local overheating. The temperature should not exceed $30^\circ C$., and should be regulated by the rate of feed of the glycerine. By observing these precautions and using a pure glycerine and acids of the prescribed quantities and concentrations the nitration of glycerine is a safe operation. In spite of this it is recommended that a vessel of five times the volume of the nitrator be placed nearby and kept full of cold water, so that in unexpected cases the charge can be quickly drowned in an excess of water and rendered safe. Addition of water to the charge is naturally to be strictly avoided.

With a cooling water temperature of $10^\circ C$. the glycerine can all be added in about ten minutes. If it is desired to determine the yields on glycerine accurately in per cent, the dropping funnel is weighed before and after the run, since the viscous glycerine hangs to the walls. The somewhat cooled charge is poured into a separatory funnel, which is covered with a glass plate. After ten minutes at the most the nitroglycerine separates sharply from the spent acids, and floats above. The rest of the charge in the lead jug is washed into a flask with about 300 cc. of water while agitating the latter, nitroglycerine still being acid. The flask is then shaken vigorously,

after being closed by a perforated rubber stopper having a bent glass tube to release any possible pressure developed and to protect against splashing out. The originally clear nitroglycerine is now milky, and is separated in a separatory funnel whose stopcock is well greased to prevent friction, and washed two or three times with 200 cc. of water, first at $30^\circ C$., then at $40^\circ C$. Then by continued shaking for two or three minutes with a 2 to 3 per cent sodium carbonate solution at $50^\circ C$. the last traces of acid are neutralized. A yellow color persists after shaking when alkalinity is reached. Then the sodium carbonate solution is removed and the nitroglycerine shaken with pure water at $40^\circ C$. The nitroglycerine so obtained is dried in a shallow dish in a calcium chloride desiccator, and after it has become clear it is weighed. The wash-waters are carefully collected and taken to the settling box of the nitroglycerine plant, or if this is impossible the oily residues are carefully separated, absorbed in sawdust, and burned, but never put into a stream, because they remain on the sides and bottom and can cause subsequent explosions. If it is desired to determine the yields accurately, the spent acids are put into a separatory funnel and allowed to stand for twenty-four hours in a cool place, and the oily matter thus separated is determined and weighed separately. The total yield amounts to about 225 grams. When using ordinary sulphuric acid it is 210 to 215 grams.

In dynamite plants laboratory nitrations are now usually made in a special glass apparatus, which will be described in the next chapter under the subject of glycerine specifications and test nitrations. It is a convenient method, closely approximating plant conditions.

If it is a question of the preparation of smaller quantities of nitroglycerine for laboratory tests without exact yield determinations, and if the above apparatus is lacking, air agitation can be used, just as in the large scale operations, and a spiral lead coil having perforations in the bottom side can be placed in the lead jug. The thermometer is then placed half way down into the acid, and the vessel in which the washing is done with air agitation covered with a suitable glass plate. On account of the acid fumes the work should be done under good ventilation.

CHAPTER III

RAW MATERIALS AND FINAL PRODUCT

The only raw materials needed for nitroglycerine are glycerine, nitric acid and sulphuric acid. The waste products are spent acid, so-called, an aqueous mixture of sulphuric acid and a little nitric acid, or after breaking down into its components (denitration) weak nitric acid and weak sulphuric acid. The larger companies making explosives, in order to reduce their costs, started a long time ago to make these raw materials in their own extensive plants, so that today many large dynamite plants maintain plants for the manufacture of glycerine and acids. To mention only one example, the Schlebusch Dynamite Plant of the Dynamit A.-G. operated during the last year of the war eight plants for the manufacture of fuming sulphuric acid by the Tentelew process, having a total capacity of 80 tons per day, four nitric acid plants, and two glycerine plants, with the help of which they provided the adjacent plants with the necessary raw materials. Such plants therefore require as raw materials for nitroglycerine only pyrites, saltpeter and crude glycerine or soap lye, and its by-products are pyrites cinder, sodium bisulphate and waste salt from the glycerine refinery.

SPECIFICATIONS FOR GLYCERINE, NITRIC ACID AND SULPHURIC ACID

Glycerine

The glycerine used by the nitroglycerine plants is the so-called "dynamite glycerine," a distilled product of the highest concentration, an article of commerce, and of the highest purity. Its purity is one of the most important factors of plant safety, in addition to perfection of apparatus. While chemically pure glycerine is colorless and odorless, dynamite glycerine is a light yellow to dark brown and usually has a slight odor somewhat resembling caramel, particularly when rubbed between the hands. The degree of color is no criterion of quality. Clear glycerine under certain conditions can be poorly suited to nitration, while deeply colored glycerine may be

suitable. The analytical methods commonly used for saponification crude, crude soap glycerine and liquors, such as oxidation with dichromate, the acetic method, the isopropyl iodide method, distillation, etc., are of little value here because fulfilling the following specifications ensures the highest quality. Analysis gives no indication of the trimethylenglycol content, which is seldom found in glycerine made from fats, and it does not show polyglycerine. For this reason the specific gravity in connection with the water content, determination of yields and behaviour on nitration, are of greater importance.

While before the war only glycerine obtained from fats and oils was of importance, which has also been the case in these last few years, in the latter years of the war the Central Powers used the so-called "Fermentol" or "Protol Glycerine" after the supplies of glycerine had been consumed and the scarcity of fats had become felt. This glycerine was that produced from sugar by a special fermentation process. This was not as pure as the regular dynamite glycerine, giving a somewhat lower yield of nitroglycerine than the latter, but otherwise quite suitable for nitroglycerine manufacture. In a crude condition it contained more or less considerable quantities of trimethylenglycol (which see), which came over in the first part of the distillation, and which when present in small amounts did not disturb the nitroglycerine operations nor affect the final product, because its nitric ester, trimethylenglycol dinitrate (which see) is also a strong explosive and at least as stable as nitroglycerine.

The specifications for dynamite glycerine are as follows:

1. *Specific gravity.* This shall be determined by a pycnometer at 15°C.; and shall be at least 1.262. When stirring cold, the formation of air bubbles must be avoided, as they escape only after long standing.

2. *Neutrality.* Shake 50 cc. of the sample with 100 cc. of distilled water and a few drops of phenolphthalein solution. A maximum of 0.3 cc. of normal acid or alkali should be required to neutralize.

3. *Residue on evaporation; ash.* The total organic and inorganic residue must not exceed 0.20 per cent, and the ash must not exceed 0.05 per cent. The residue is determined by carefully evaporating 5 to 10 grams of the glycerine in a platinum dish in a sand or air bath at 160 to 180°C. with the addition of several successive small amounts of water to avoid the formation of difficultly volatile polyglycerines, which can also be easily formed if too large samples are used for the analysis, such as 25-gram samples. For the simultaneous analysis of several samples a round, heavy iron plate 4 to 5 cm. thick, heated by burners, and having round depressions for the platinum dishes, is very

convenient. A low-melting alloy is in the central depression, with a thermometer in it. After constant weight is obtained the inorganic residue is determined by carefully heating to redness.

4. *Water content; presence of polyglycerines.* Frequently the water content of dynamite glycerine is also determined, although this takes a great deal of time, and is only approximate. A diglycerine (which see) and polyglycerine content, which can be formed by a local overheating during the distillation, raises the specific gravity and may affect the yields and nitroglycerine separations adversely. A high specific gravity can therefore, by the simultaneous presence of water and polyglycerine, apparently represent a higher glycerine content than is actually present, while on the other hand, in the determination of the non-volatile residue the polyglycerines are hydrated by the addition of water and can be evaporated. Since 100 per cent glycerine has a specific gravity of 1.264, and diglycerine 1.33, 10 per cent diglycerine raises the specific gravity of a glycerine 6.6 units in the third decimal place. On the other hand, glycerine produces theoretically 246.7 per cent of nitroglycerine, and diglycerine only 208.4 per cent of tetranitrodiglycerine. Therefore 10 per cent of diglycerine reduces the nitroglycerine yield 3.8 per cent. Diglycerine and polyglycerines have been made purposely in order to produce low-freezing nitroglycerine (see chapter on non-freezing dynamites), and the more difficult washing on account of the formation of emulsions has been to a certain extent overcome.¹ The statement that the quality of the nitroglycerine is injured by a diglycerine content of the glycerine, as in *Chemiker Zeitung.*, page 41, 1912, is not true, since nitroglycerine contains 3.5 per cent more oxygen than is necessary for complete combustion, and tetranitrodiglycerine 18.5 per cent too little, so that a mixture of 85 per cent nitroglycerine and 15 per cent tetranitroglycerine still contains sufficient oxygen for complete decomposition and maximum heat of explosion. The presence of a few per cent of di- and tri-glycerines is of no practical importance, provided that they do not mask a higher water content by their specific gravity, which latter is of importance in that each per cent of water means a drop in yield of 2.3 per cent aside from the injurious diluting action on the nitrating acids, which exerts a harmful effect only with a high water content in the glycerine.

Determination of the water content of glycerine. The water content of glycerine can be determined by allowing a small quantity of glycerine to stand in a thin layer over sulphuric acid in vacuo until constant weight is obtained. Since glycerine itself retains water strongly it does not release it all. Ten grams of glycerine can be heated in a loosely covered weighing bottle for one hour at 90°C., a circular piece of filter paper being placed between the glass and the cover. The loss of weight is determined hourly until it becomes constant and small.

5. *Mineral impurities.* Glycerine must contain only traces of chlorides,

¹ Nitroglycerines containing 23 to 25 per cent of tetranitrodiglycerine have been used in the United States continuously since 1912 for low-freezing dynamites, the emulsion formed during washing being broken up by washing with warm, common salt solution.—TRANSLATOR.

sulphates, calcium salts and arsenic, derived from the reagents used in the preparation of the crude glycerine and carried over with the distilled glycerine by improperly conducted distillation.

6. *Sugar and glucose* prove deliberate adulteration, and should not be present.

7. *Absence of reducing substances.* Equal volumes of glycerine and a 10 per cent silver nitrate solution are mixed, and after standing for ten minutes in the dark should show no black cloud. It is recommended also that glycerine be mixed with an equal volume of Fehling's solution, such as is used for sugar determinations, and a flask rapidly and completely filled with this, so that no air remains between the stopper and the liquid. After standing for twelve hours there should be no reduction.

8. *Absence of albumins.* With a lead acetate solution there should be no precipitate, or at the most only an opalescence.

9. *Absence of fatty acids.* Fatty acids should be absent, or present only in traces. Volatile fatty acids are recognized by the ester-like odor formed on heating with alcohol and strong sulphuric acid. Higher fatty acids, like oleic, are determined by diluting the glycerine with twice its weight of water, adding nitrous acid and heating for two hours on a water bath, giving a precipitate if present. Good dynamite glycerine as a rule contains at least 99 per cent glycerine and less than 1 per cent water.

Test nitration

A dynamite glycerine can conform in general to the above specifications and yet show undesirable reactions in the manufacture of nitroglycerine, e.g., too slow a separation from the spent acid, incomplete direct separation and slow after-separation, the formation of emulsions, and poor settling from the washes, and last but not least low yields. Mere traces of impurities of certain kinds can be the cause of this. For this reason the dynamite plant, in addition to the chemical and physical tests, places great reliance upon the so-called test nitration. Yield determinations on a factory scale are seldom made, since the use of plant apparatus gives exact results only as an average of a long series of nitrations, and consequently gives a fairly satisfactory idea of yields only with a large quantity of glycerine. For this reason a test nitration in the laboratory, with exact determination of yields, is preferable. It is best not to work with too small quantities, because then the effect of the difficultly avoidable loss of the small drops clinging to the walls is too serious a factor. Moreover, measurement of the washed nitroglycerine, often recommended, is not sufficiently accurate. The moisture content and the possible error of the measuring device can affect the results.

The method of measuring nitroglycerine, unwashed and directly after separation, as given in Guttman: *Die Industrie der Explosivstoffe*, page 95, is quite inaccurate because the nitroglycerine then contains appreciable amounts of the concentrated acids. It is better to weigh the nitroglycerine after drying in a desiccator, on a balance sensitive to 0.01 gram.

The apparatus most commonly used for this purpose is the glass, pear-shaped nitrator shown in figure 1, usually holding a charge

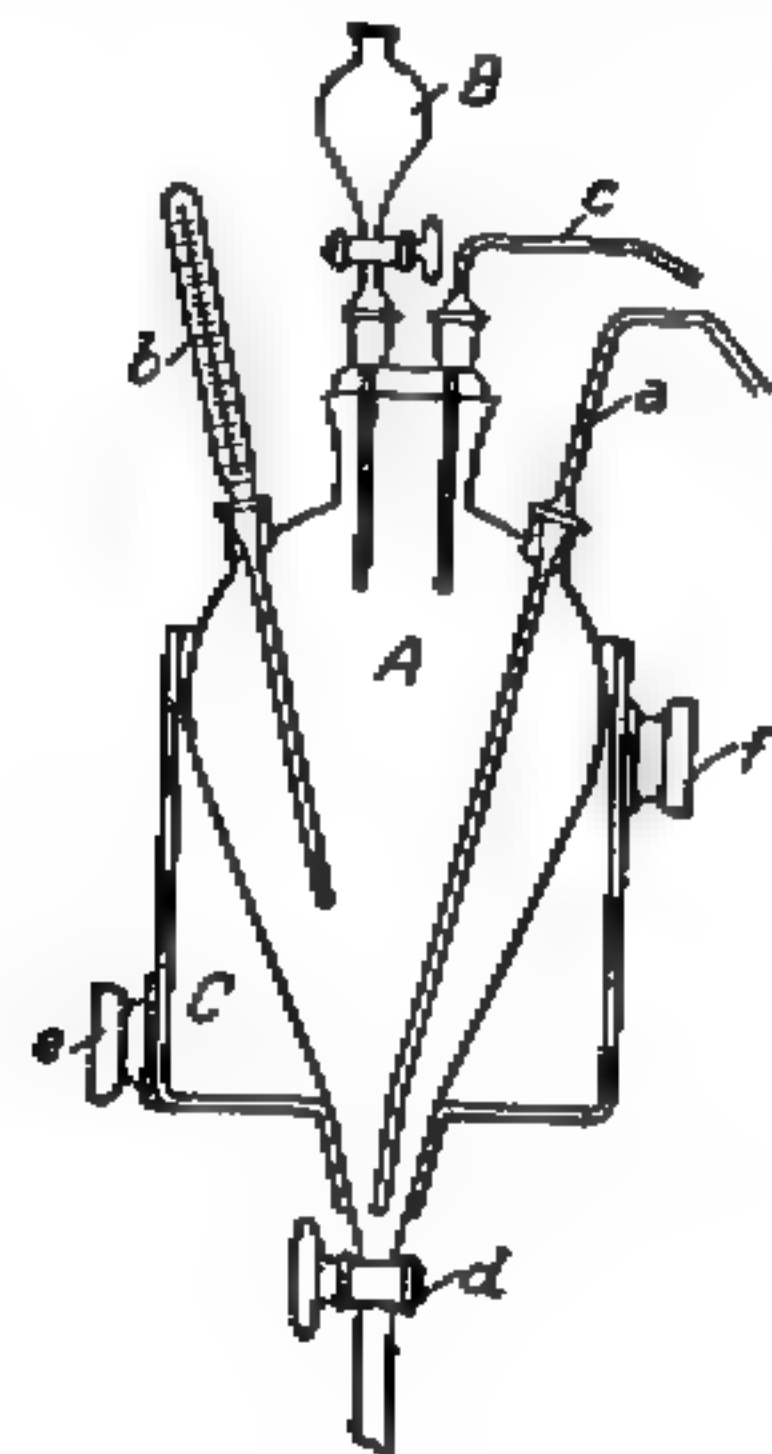


FIG. 1

FIG. 1. GLASS NITRATING FUNNEL FOR TEST NITRATIONS

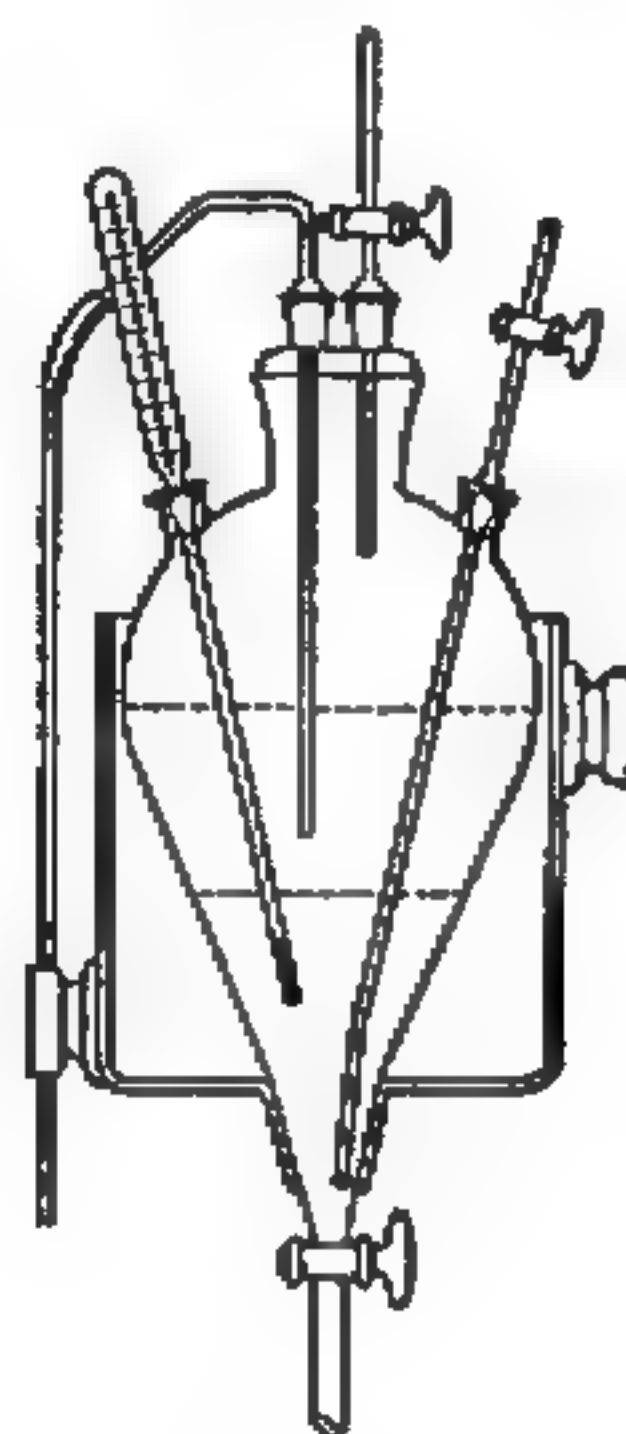


FIG. 2

FIG. 2. IMPROVED GLASS NITRATING FUNNEL

of 100 grams of glycerine, corresponding to about 225 grams of nitroglycerine.

The apparatus consists of a nitrator, A, with a glycerine dropping funnel, B, fitting into the cooling jacket, C, by a ground glass joint, the jacket having water inlets and outlets, e and f, which can be filled as desired with crushed ice, water or cooling mixtures, to maintain the proper temperature. The bent glass tube, a, reaching almost to the bottom stopcock, d, is used to introduce the compressed air. The thermometer, b, is inserted from the side, and the acid vapors evolved by the current of air escape through the vent pipe, c. All parts of the apparatus have ground joints. Washing of the nitroglycerine is also done in the same apparatus by a current of air. To prevent wash-water

being separated from the nitroglycerine on drawing off the latter Novak,² altered it by using a three-way stopcock at the top, and a syphon and stopcock. The syphon ends above the nitroglycerine layer, the height of the latter being determined by trial. After the nitration is finished and the spent acid drawn off the dropping funnel is replaced by an exit pipe attached by a rubber tube to a vessel filled with water, and the required quantity of water is added to the acid charge while being vigorously agitated. After settling a slight pressure is put on the liquid by means of the tube and a piece of rubber tube, after removing the air inlet and exit pipes, so that the wash-water is forced through the syphon (fig. 2).

The method of operating this device is as follows: After the proper preliminary cooling of the acid the latter is vigorously agitated by a current of air, regulated by the stopcock, the air current passing through a calcium chloride tower to dry it and prevent the water in the air from getting into the nitrating acid. The warm glycerine is then allowed to drop in rapidly until the desired or allowable maximum temperature is reached, not over 30°C., and then the rate of feed of the glycerine regulated according to the efficiency of cooling, maintaining the temperature within narrow limits, say plus or minus 1°C. The time of nitration depends upon the temperature of the cooling water, and if the latter be +10°C. and the nitrating temperature +25°C., the amount of glycerine fed in may be 100 grams in about twenty minutes. The separation takes place smoothly in a maximum of ten minutes, after which time a sharp line between nitroglycerine and acid should form without flaky separation and without slimy particles floating on the oil. Likewise, in the subsequent washing a slightly but not markedly milky nitroglycerine should separate without formation of an emulsion or foam. If these conditions are not met objection should be made to the glycerine, as it is not adapted to the manufacture of nitroglycerine and must be redistilled. Many, particularly if inexperienced, wash with too much water. This is improper because nitroglycerine, although difficultly soluble, is not insoluble in water, particularly when warm, so that the yields are affected unfavorably by too much water and no longer correspond to the plant results obtained with smaller but sufficient quantities of water. A quantity of water equal to the volume of the nitroglycerine is sufficient. Exact yield determinations should also have regard to the after-separation, which may amount to 0 to 5 grams, depending upon whether the oil is allowed to stand in the separator a long or a short time, and upon the quality of the glycerine. After-separation burettes with a bulb at the bottom for direct reading of the after-separated oil in cubic centimeters have not been satisfactory because a part of the oil clings to the walls of the bulb and does not rise up into the burette. Separatory funnels are preferable.

If compressed air is not available, air can be drawn through the acid by a water jet pump, the acid vapors being taken away by the pump. An empty, intermediate flask with a stopcock should be placed in the line next to the pump to prevent water from sucking back.

² *Z. Schiess- und Sprengstoffw.*, 1, p. 191.

In many plants the following regulations are in use for the greatest possible accuracy in determining the yield to be expected from a given glycerine:

Glycerine. About 101 grams are weighed into a small separatory funnel. Depending upon the temperature of nitration and the desired rate of feed, the glycerine is warmed up somewhat (30 to 45°C.) to make it more fluid. After all the glycerine is fed in, the funnel is again weighed, and the glycerine consumed determined by difference.

Nitrating acids. Quantity, 630 grams. Composition: HNO_3 , 40 per cent; H_2SO_4 , 59 to 60 per cent; H_2O , 0 to 1 per cent. Quantity and composition of the acids should follow closely plant conditions.

Nitrating temperature. These should parallel plant practice, for example, if the plant uses water for cooling, nitration should be at 25 to 30°C. If the plant uses artificial refrigeration with brine in the coils at -10°C ., the cooling jacket of the apparatus is filled with an ice-salt mixture and nitration made at 14 to 15°C.

Agitation. Most apparatus is fitted for compressed air agitation. The aim is a thorough but not excessive mixing, so that the air current will not carry away too much nitric acid during the nitrating period. The vapors evolved are carried away by a glass tube to a good draught, or passed out of the room through a hole in the window.

If compressed air is not available the nitrator can be stirred mechanically by a turbine or by hand. In such a case nitration is carried out in an open lead vessel, stirred by a thermometer, which is read frequently after the flow of glycerine has been temporarily stopped. With mechanical agitation a 1 per cent higher yield is usually obtained than when using compressed air.

Separation. After all the glycerine has been added the agitation is continued for one or two minutes, the cooling mixture removed from the jacket or the cooling water shut off, and the oil allowed to separate from the acids at 25° or 10°. It is better, even with rapid separations, to allow the charge to stand for thirty minutes to avoid after-separation as much as possible.

Stabilization. After complete separation the acid is slowly and carefully run out into an open separatory funnel, the latter covered by a glass plate and left in a cool place for the after-separation, which is determined on the following day.

The nitroglycerine is run into an Erlenmeyer flask containing 100 cc. of cold water, while shaking constantly, the apparatus washed out with a further 50 cc. of water, the whole poured back into the apparatus, and agitated with an air current for five minutes. This preliminary wash with cold water is followed by two more washes, each with 100 cc. of water at 30° and 40° respectively, and lasting for five minutes, the jacket being filled with lukewarm water at a temperature suitable to maintain the desired temperature of the charge. It is then agitated for ten minutes with 100 cc. of a 3 to 4 per cent sodium carbonate solution at 40°C., and finally with 100 cc. of pure water at 30 to 40°C. for five minutes.

All wash-waters are collected in a separatory funnel and allowed to clarify therein, a glass rod being used to collect the oily drops from the walls and make them coalesce on the bottom.

After proper settling, the main quantity of nitroglycerine is drawn off into a weighed glass dish and put into a desiccator. On the next day, after becoming clear of emulsified water from the washings, it is weighed.

The yield is made up of the following components:

1. Direct yield. The main quantity of nitroglycerine.
2. After-separation. On the next day, or in case of haste being necessary, after some hours, the spent acids are carefully drawn off, the nitroglycerine on the surface is washed with water without shaking, and run into a weighed dish. From this weight 10 per cent is deducted for the concentrated acids in the oil which has not been shaken with water. Since here it is usually a matter of only a few grams, this empirical practice is usually sufficiently accurate.

3. Mechanical losses. Finally the nitroglycerine, separated by clarification of the wash-waters, is drawn off, weighed and added to the yield.

The figure obtained, in grams, is divided by the quantity of glycerine used, giving the per cent yield based upon glycerine. By following the above directions agreement between two parallel tests to a few tenths of a per cent of the glycerine can be obtained.

The process described can be applied to yield determinations of nitroglycol without alteration, because the stoichiometrical relations of glycerine and glycol versus nitroglycerine and nitroglycol are almost the same.

The nitroglycerine yield so determined is always less than that obtained on a plant scale with the same raw materials, but with more careful work it is generally not more than about 1 to 1.5 per cent low. This is because in the laboratory tiny drops escape exact determination, while on the plant scale no trace of nitroglycerine escapes, all being collected and returned to the washers. Moreover, in plant practice the nitroglycerine is usually weighed with a moisture content of 0.3 to 0.5 per cent, which compared to the dry product corresponds to a 1 per cent higher yield on the glycerine.

Under the above conditions the best dynamite glycerine gives a laboratory yield of 225 to 226 per cent at a nitrating temperature of 30°C., and 228 to 229 per cent at 15°C.

In order to carry out the test nitration in the simplest and most convenient way and as rapidly as possible Hofwimmer² proposed a so-called nitrating burette, in which a small quantity of nitroglycerine was made, and after standing for fifteen minutes its volume was determined exactly by means of a precision

² Chem. Ztg., 1912, p. 41.

burette. Since this method and apparatus was intended to make possible an exact evaluation of different kinds of dynamite glycerine, and has been recommended in recent books,⁴ a critical consideration of its real worth is justified. The apparatus (fig. 3) consists of a 15 cc. measuring tube divided into tenths or twentieths of a cubic centimeter, so that hundredths can be estimated. Compressed air is introduced through the bottom stopcock to stir the mixture during the addition of the glycerine. At the upper end the measuring tube swells out to a bulb, which is surrounded by a cooling jacket. From a separatory funnel containing 10 grams of glycerine between two graduations, and

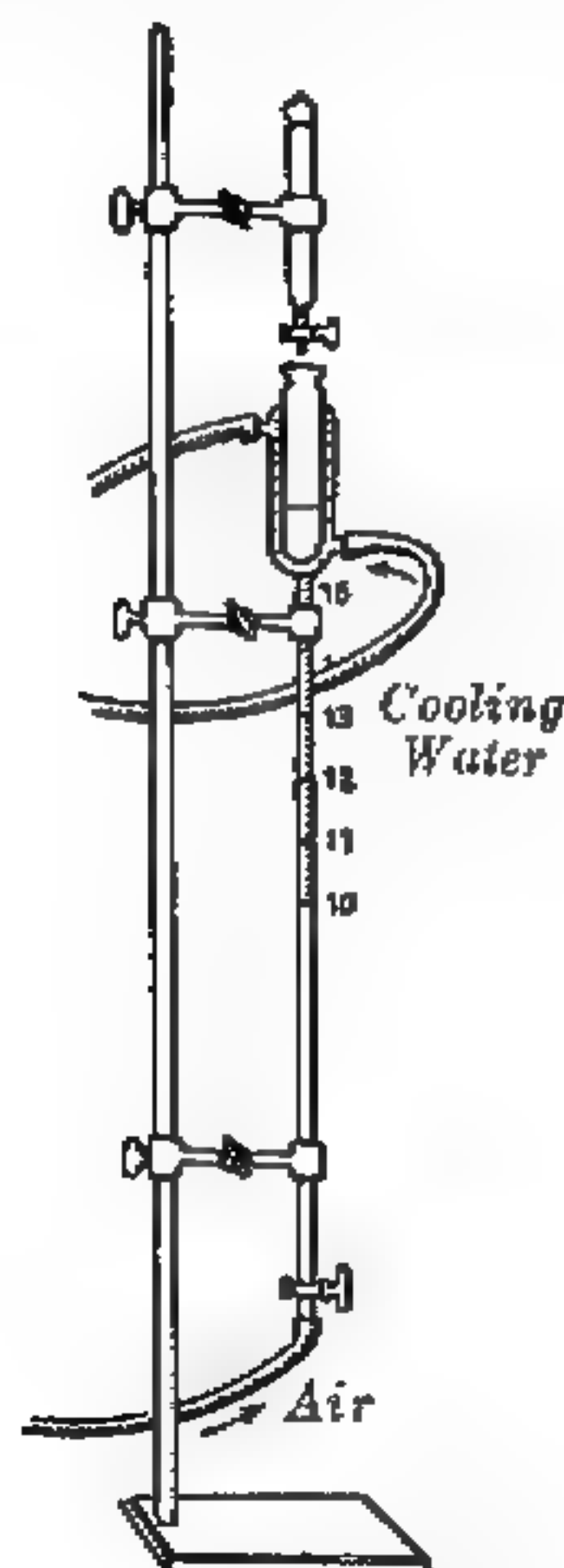


FIG. 3. NITRATING BURETTE

which is weighed before and after use, glycerine is added to the acid surrounded by the water jacket. The amount of acid is 60 to 65 grams. The temperature is not measured because of the small quantities involved and the abundant cooling and uniform conditions. After the separation, which should be complete in fifteen minutes, the acid is drawn off until the layer of oil reaches the upper zero mark, and the volume of the nitroglycerine read off. For comparison of different kinds of glycerine naturally a stock of uniform nitrating acid is used. Since real yields of pure nitroglycerine are not determined, but rather the volume of nitroglycerine contaminated by suspended and dissolved acids, there must first be determined the volume of acid nitro-

glycerine obtained from 10 grams of a pure, anhydrous glycerine. This latter figure is the standard for testing other varieties.

Each degree of lower volume obtained with other kinds of glycerine signifies a corresponding reduction in the value of the glycerine under consideration. It should be noted that the weighing of the glycerine on the analytical balance, which is claimed to be of particular advantage as compared to rough work with 100 grams of roughly weighed glycerine, is of no advantage insofar as it exceeds 0.01 gram, because the volume can only be read to 0.01 cc. Rough balances are also able to weigh to 0.01 gram. Although the separation is usually complete after fifteen minutes, appreciable quantities of nitroglycerine separate subsequently, varying with the different kinds of glycerine, so that when the

TABLE 1
Glycerine determinations by the nitrating burette

KIND OF GLYCERINE	VOLUME FOR 10 GRAMS GLYCERINE	YIELD BY VOLUME	ACTUAL YIELD ON 100 GRAMS	GLYCERINE VALUE
	cc.	per cent	per cent	per cent
Chemically pure anhydrous	15.65 } 15.49 } 15.57	229.4*	229.4	100.0†
Dynamite glycerine number 1	15.25 } 15.15 } 15.20	224.0‡	227.4	97.65§
Dynamite glycerine number 2	15.42 } 15.36 } 15.39	226.8	225.0	98.9
Dynamite glycerine number 3	14.65 } 14.56 } 14.60	215.2	212	93.8

* Obtained.

† Assumed.

‡ Calculated.

§ By volume.

acid is run off there must be a wait of at least one hour to afford a true indication, because in commercial practice the after-separated oil also is recovered. Furthermore it is a long time, as a rule several hours, before the oil volume becomes constant and can be read, since it is constantly separating the suspended acid contained in it and so is contracting. Here also at least one hour must pass, so that the whole determination takes about two and a half hours. In this period an exact analytical determination can be made, whereas in any case the after-separation can only be determined after twelve hours, or on the next morning. Assuming a sufficient accuracy, the Hofwimmer method has the advantages of great simplicity and little labor, so that, assuming absolutely uniform burettes, a number of simultaneous determinations can be made by one person.

⁴ Stettbacher, *Schiess- und Sprengstoffe*, 1919, p. 112.

However, according to tests made by the author, the accuracy of the method cannot be compared with that obtained by weighing the purified, dry nitroglycerine. There is also the disadvantage that the behaviour of the nitroglycerine during nitration and particularly during separation cannot be observed as well with the 10 grams as with the 100 grams. In the latter case, with some practice, an agreement between two parallel determinations to 0.5 grams of nitroglycerine, corresponding to 0.2 per cent glycerine, is readily obtained. In the nitrating burette 0.15 cc. of nitroglycerine corresponds to 1 per cent glycerine, and the limit of error of parallel determinations is not much lower. Comparisons of high grade dynamite glycerine by the burette gave values not agreeing with actual yields obtained by weighing, although glycerines of appreciably lower grade gave considerably lower volumes of oil. The method does not take into consideration the different tendencies of glycerines to emulsify with acids and retain the latter in suspension, and therefore does not give fine distinctions, and can serve only as a makeshift.

The nitroglycerine made in the experiments is used in the nitroglycerine plant, otherwise it must be immediately destroyed. For this purpose it is mixed with an excess of sawdust by means of a horn spatula. This mixture is then ignited on an iron plate and burns without danger.

Although the melting point of glycerine is comparatively high, 17°C ., it can usually be subjected to rather low temperatures without freezing. Like most viscous liquids, and like nitroglycerine, it exhibits the phenomena of supercooling to a marked degree. However, if it is stored for a long time in large quantities in the open in cold times of the year, or in an unheated place, it frequently crystallizes to a solid mass of crystals which melt very slowly and remain solid in the spring of the year for weeks at a time at temperatures around 20°C . For this reason large quantities of it are stored in vats heated by steam or hot water, which vats must be closed on account of the hygroscopicity of the glycerine. Often steam heated rooms, in which the drums of glycerine are placed several days before use, are used. The customary iron drums for storing and transporting glycerine usually hold from 450 to 500 kg., and are provided with an iron screw plug and reinforcing bands. Wooden casks, lined with glycerine pitch, formerly used to transport glycerine, gave large losses in summer, since glycerine has the peculiar property of sweating badly through fine cracks and openings, apparently through capillary action.

Nitric acid

The nitric acid should be as concentrated as possible. Its specific gravity should be 1.5 (48°Bé) and the monohydrate content exceed 90 per cent. The weaker the nitric acid the stronger must be the sulphuric acid (or oleum), or the greater the quantity of the latter, in order to give the mixed acid the required concentration.

A nitrous acid content of the nitric acid does no damage, either to the nitration or the quality of the final product. Also, as tests have shown, it is without effect upon yields, provided the required quantity of nitric acid monohydrate is present in addition to the nitrous acid. The nitrous acid in the mixed acid is chemically combined with the sulphuric acid, and when in this condition it is not an oxidizer at the given concentration of acids and at the nitrating temperatures used, and takes part in the reaction only in the sense of 2 molecules of NO_2 with 1 molecule of H_2SO_4 yielding 1 molecule of free HNO_3 and 1 molecule of HNO_2SO_3 (nitrosylsulphuric acid), the latter going through the process as completely inert matter and only becoming burdensome on washing the acid oil, or in denitration of the spent acids. A high content of nitrous acid in the nitric acid is therefore undesirable. Commercial nitric acid contains a maximum of 1 per cent nitrous acid, corresponding to 0.4 per cent in the mixed acid.

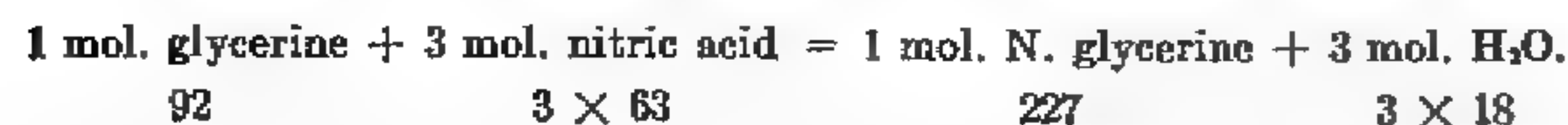
Sulphuric acid

Just like the nitric acid, the sulphuric acid should be of the highest possible concentration. Up until the close of the last century the so-called English sulphuric acid, with a specific gravity of about 1.84 or 66°Bé and containing 96 per cent monohydrate, was used. Since that time most of the large explosive plants have made their mixed acid from fuming sulphuric acid (oleum), obtained by the so-called anhydride process (contact process) and containing 20 to 40 per cent free SO_3 . A lead sulphate content in this sulphuric acid, which is of little importance in the manufacture of nitrocotton, is undesirable in this case, because on mixing with nitric acid the lead sulphate precipitates in fine crystals, which render the mixed acid cloudy for a long time, and only settle to the bottom slowly as lead mud. This turbidity hinders the separation of the nitroglycerine. It is therefore advantageous to prepare large stocks of mixed acid and give them time to settle, and also to draw the mixed acid out of storage tanks not

from the bottom but from some height above the bottom, leaving the lead mud behind.

Mixed acid and its preparation.

Proportions; ratio of acid to glycerine. The chemical equation is:



so that 92 parts of glycerine and 189 parts of nitric acid give 227 parts of nitroglycerine, or 100 parts of glycerine and 205.4 parts of nitric acid give 246.7 parts of nitroglycerine.

In actual practice, however, a certain excess of nitric acid is necessary to complete the reaction, because otherwise toward the end of the reaction the velocity will fall considerably on account of the great dilution of the HNO_3 molecules in the mixture, and finally the reaction will cease, since as in every esterification, it is reversible, splitting off pure nitric acid from nitroglycerine and sulphuric acid.

The sulphuric acid must be present in such quantities that up to the end of the reaction a composition is maintained which renders possible the formation of nitroglycerine. *The required quantity of sulphuric acid is therefore merely dependent upon the concentration of the sulphuric and nitric acids.*

In the course of time several more or less advantageous compositions and ratios have been tried. For an historical review see Guttman: *Die Industrie der Explosivstoffe*, page 397, 1895. Sobrero used 1 volume of glycerine to 2 volumes of nitric acid of 43° Bé and 4 volumes of sulphuric acid of 66° Bé, or 100 parts by weight of glycerine, 226 parts of 71 per cent nitric acid and 584 parts of sulphuric acid, or altogether 810 parts of mixed acid. Since he used only 43° nitric acid his mixture was too low in nitric acid to give a theoretical conversion of glycerine to nitroglycerine. It did not even contain the theoretically required quantity of HNO_3 .

When the manufacture of nitroglycerine on a large scale was commenced 1 part of nitric acid was usually mixed with 2 parts of sulphuric acid, but it was found later that less sulphuric acid could be used, and then a mixture of 3 parts of nitric acid and 5 parts of sulphuric acid was commonly used. This mixture had the following percentage composition:

Sulphuric acid.....	per cent 62.5
Nitric acid.....	37.5

Assuming a 93 per cent nitric acid and a 96 per cent sulphuric acid, it is possible to obtain about the following composition of monohydrates and water:

HNO_3	per cent 35
H_2SO_4	60
H_2O	5

Then 700 to 800 parts of such an acid are taken for 100 parts of glycerine. The use of fuming sulphuric acid (oleum) is of recent date, to the production of which the large dynamite plants turned at the beginning of the present century, the first of them being Krümmel a.d. Elbe, Ardeer at Glasgow, and Modderfontein in Transvaal. The oleum usually contained about 20 per cent of free anhydride. Naturally, with an acid of such a high concentration, less is required to attain the same degree of dehydration, and it is necessary to mix 3 parts of nitric acid with only 4 parts of such oleum. For example, assuming a nitric acid containing about 93 per cent monohydrate and an oleum of about 18 per cent free SO_3 or 104 per cent monohydrate, i.e., 100 parts of oleum and 4 parts of water give 104 parts of H_2SO_4 , the composition of a mixture of 3 parts of nitric acid and 4 parts of oleum, or 43 per cent nitric and 57 per cent oleum, can be calculated as:

HNO_3	per cent 40.0
H_2SO_4	59.5
H_2O	0.5
	<hr/>
	100.0

If a somewhat weaker nitric acid is available an oleum richer in anhydride is used. Monohydrate mixtures of similar composition, without any water in them, are today considered as most advantageous by modern plants for the manufacture of nitroglycerine, and to attain this high concentration is always the effort of the acid department of the explosives plant. The use of oleum has the advantage of giving an appreciably higher yield. Before its use the yield of nitroglycerine in favorable cases amounted to 210 to 215 per cent of the glycerine, but today 225 per cent and above is readily obtained. For

further details on yields and economy see the section under Economy of Process, at the end of the description of the manufacture. In the literature these proportions were only recognized some years later by the patent application of Nathan and Rintoul,⁵ who obtained 230 parts of nitroglycerine from 100 parts of glycerine and about 620 parts of an anhydrous mixed acid containing about 42 per cent HNO_3 . Also a still lower acid ratio of about 555 parts of an anhydrous acid containing 47.7 per cent HNO_3 , with 100 parts of glycerine was proposed, and said to give a 229 per cent yield.⁶ For the preparation of an anhydrous acid of this composition an oleum containing above 30 per cent free SO_3 is in any case necessary, which usually cannot be prepared directly by the so-called contact process.⁷

Preparation of the mixed acids. The mixing of nitric acid with sulphuric acid is done in iron or lead containers.⁸ The development of heat is considerable, and varies according to whether ordinary or fuming sulphuric acid is used. In the latter case it is four times as great as in the former, so that the mixing of nitric acid and oleum requires special cooling devices to prevent loss of nitric acid by evaporation. A homogeneous mixture is obtained without any special agitation if the sulphuric acid is allowed to flow from above into the whole quantity of nitric acid. The mixing is completed on further transportation through pressure tanks and acid pipes with gradual cooling. The temperature rise amounts to 20 to 30°C.

For mixing nitric acid and oleum special apparatus, provided with abundant cooling by lead coils⁹ or less frequently by cooling jackets is used. Mechanical agitation is little used¹⁰ and air agitation is

⁵ French patent 366593, *J. Soc. Chem. Ind.*, Nathan and Rintoul, 1908, p. 143-205; *Z. Schiess- u. Sprengstoffw.*, 1908, p. 314-6, British patent 6581, 1906.

⁶ Today in Germany a mixed acid containing 50 per cent HNO_3 and 50 per cent H_2SO_4 is rather commonly used, or a ratio of 500 kgm. of acid to 100 kg. of glycerine. The yield obtained is 234 to 235 per cent.—RECENT NOTE BY THE AUTHOR.

⁷ This is being done at present in the United States.—TRANSLATOR.

⁸ Only steel vessels are used in the United States.—TRANSLATOR.

⁹ For such strong acids iron or steel coils are always used in the United States.—TRANSLATOR.

¹⁰ Mechanical agitation, or pumping out of the bottom and returning to the top of the tank is in practically exclusive use in the United States.—TRANSLATOR.

usually avoided because considerable quantities of nitric acid are blown out and can only be recovered as a weak acid in towers. This causes the initial calculation of the mixed acid to be somewhat uncertain. The best arrangement is that where the nitric and sulphuric acids run in simultaneously through opposite pipes, giving sufficient mixing.¹¹ The weighed or measured nitric and sulphuric acids are in adjacent containers, the oleum in a wrought iron tank, the nitric in a stoneware vessel, and from here they flow through pipes and regulating valves into a lead mixing tank provided with numerous cooling coils and a thermometer. After the mixing is completed, the temperature not being allowed to rise above 40°C., the mixed acid is run into a pressure tank, from which it is forced to the storage tanks.¹² From these a sample is taken and a proper addition of either nitric or sulphuric acid is made according to the analysis. Weighing of the components and exact maintenance of working conditions often make correction unnecessary. A small condensing tower is connected with the mixing tank, but with proper cooling in the latter the amount of nitric acid obtained from the tower is small. The storage tanks are made as large as possible, so that they will hold a supply for several days and allow the fine crystals of lead sulphate formed during the mixing to separate as completely as possible. Storage tanks of 60,000 to 80,000 kg. are no rarity. Once intimately mixed the acids can never separate, since they are mutually soluble as well as chemically combined with one another, as is evident from the great heat developed during the mixing, which occurs not only when sulphuric acid is mixed with hydrous nitric acid, but also on mixing anhydrous monohydric acids or anhydrous nitric acid with sulphuric acid containing free SO_3 .

¹¹ In the United States the strong nitric acid coming from the condensers is run into an iron tank partly filled with oleum, and the mixture circulated by a centrifugal pump through a cooling coil of iron pipe placed in a shallow tank of water. This iron equipment lasts for many years with such strong acids. The centrifugal pump is immersed in the acid in the tank, no packing glands being required, with only the delivery pipe emerging from the tank.—TRANSLATOR.

¹² In the United States centrifugal pumps have largely displaced compressed air as a means of forcing acids through pipes, in order to avoid the large consumption of compressed air necessary, and the formation of fumes when the air is released, and the necessity of providing numerous absorption towers.—TRANSLATOR.

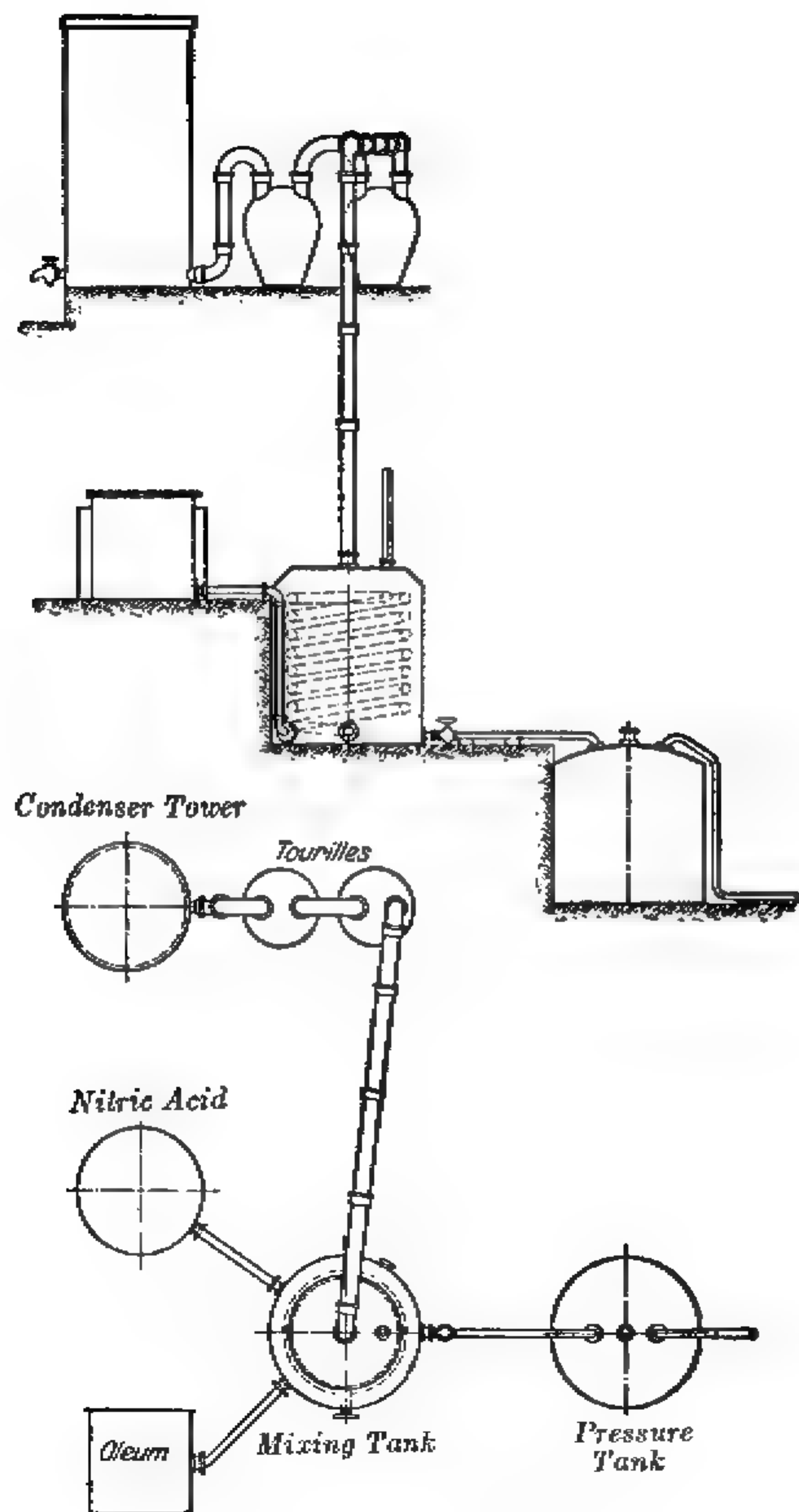


FIG. 4. DIAGRAM OF ACID MIXING PLANT

On suddenly mixing 40 grams of 99 per cent nitric acid with 60 grams of 20 per cent oleum the temperature rises about 80°C ., e.g., from 15° to 95° , with boiling and partial volatilization of nitric acid. On the other hand, if 40 grams of 99 per cent nitric acid is mixed with 60 grams of 96 per cent sulphuric acid the temperature rises only about 20° , e.g., from 15° to 35° . It can be assumed that in such a mixture the nitric acid is present in the form of its anhydride, i.e., that the enormous affinity of oleum to take up water dehydrates even nitric acid monohydrate. As a matter of fact, however, on heating mixed acid nitric acid anhydride does not distil off, but a 99 to 100 per cent nitric acid.

Analysis of mixed acid. The composition and uniformity of the mix is determined by taking samples from the top and bottom of the storage tank, which must give concordant results on analysis. The analysis of mixed acids is done in dynamite plants by two methods, each of equal value for fresh mixed acids.

The nitrometer method. In one sample the total acid is determined by $\text{N}/2$ KOH , and calculated as sulphuric acid. In a second sample the nitric acid is determined by a Lunge nitrometer (fig. 5), the nitric acid calculated to sulphuric acid, and the latter value subtracted from the total acidity, giving the sulphuric acid content. The difference from 100 per cent is water.

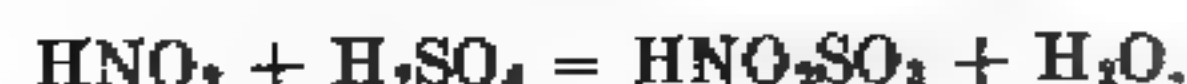
For example:

Total acidity.....	90.1 per cent H_2SO_4
minus HNO_3 , 40 per cent determined =	31.1 per cent H_2SO_4
	<hr/>
	= 59.0 per cent H_2SO_4
	40.0 per cent HNO_3
	1.0 per cent H_2O
	<hr/>
	100.0 per cent

The nitrous acid is not determined if its percentage in the nitric acid used is known. If it is to be determined in purchased mixed acid a few grams of the latter are put into a large excess of water and titrated with $\text{N}/10$ permanganate solution until the red color persists for one minute, or better, the concentrated mixed acid is allowed to run out of a burette into a definite quantity, e.g., 25 cc., of the $\text{N}/10$ permanganate solution diluted with water and acidified with sulphuric acid, until the color is discharged. In order to determine the quantity of acid consumed its specific gravity must be known. To determine this exactly 10 cc. of the acid is run into a tared weighing bottle and weighed. The nitrous acid is usually calculated as NO_2 .

100 cc. $\text{N}/10$ KMnO_4 solution = 0.46 grams NO_2 or 0.19 grams N_2O_4 .

The nitrous acid is reported as such or calculated to nitrosylsulphuric acid, HNO_2SO_3 , which is justified, wherein $2\text{NO}_2 + \text{H}_2\text{SO}_4 = \text{HNO}_2\text{SO}_3 + \text{HNO}_3$, or only one-half of the calculated NO_2 can be considered as inert. The titration can also be calculated to HNO_2 , where 100 cc. of N/10 KMnO_4 solution = 0.235 grams HNO_2 , and the recalculation to nitrosylsulphuric acid becomes:



The nitrous acid, as well as half of the calculated NO_2 , is calculated to HNO_3 and deducted from the HNO_3 found by the nitrometer.

The nitrometer,^{13,14} Fig. 5, consists of a receiver *a*, measuring tube *b*, with a shaking bulb *c*, connected with the leveling tube *e*, by a thick walled capil-

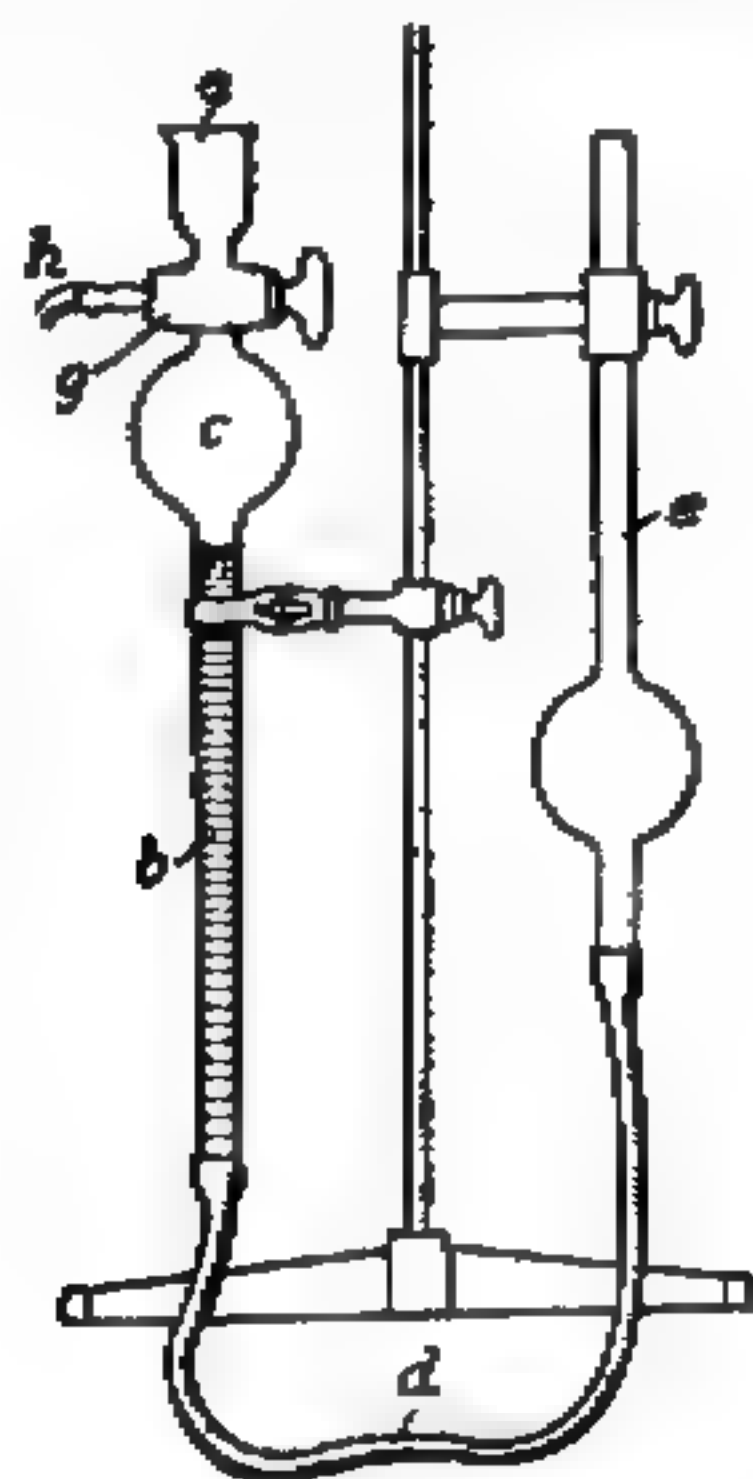


FIG. 5. NITROMETER

lary tube *d*. Underneath the measuring tube it is an advantage to have a small bulb to prevent the sulphuric acid getting into the rubber tube. The leveling tube also has a bulb at the bottom, or else is so wide that it can easily receive all the mercury displaced from the shaking bulb and measuring tube. The shaking tube holds about 100 cc., and the measuring tube is divided into tenths between the 100 and 150 cc. marks. A eudiometer without a bulb, containing 50 cc., is less suitable for exact determinations.

The method of analysis, which is based upon the reduction of HNO_3 by mercury and concentrated sulphuric acid to NO and measurement of the NO gas, is as follows:

¹³ See Lunge-Berl, *Chem.-techn. Untersuchungsmethoden*, vol. 1.

¹⁴ A compensating bulb, filled with dry air, to correct for barometer and temperature automatically, and standardization of the nitrometer by pure KNO_3 , is a great help, and widely used in the United States.—TRANSLATOR.

The receiver is filled from a pipette with a quantity of mixed acid corresponding to a volume of NO between 110 and 140 cc., about 0.8 grams in the case of 40 per cent HNO_3 , the mercury being wet with concentrated sulphuric acid, and the mixed acid drawn in from the receiver by reduced pressure. After the receiver has been washed out three or four times, first with a large quantity and then with smaller amounts of sulphuric acid, the apparatus is shaken constantly for several minutes until the volume of gas developed becomes constant. The gas is then brought to approximately atmospheric pressure, a thermometer hung on the stand, and after the temperature has become equalized, for example in about fifteen minutes, it is again adjusted, and the gas volume, temperature and barometer read.

The solubility of nitric oxide in concentrated sulphuric acid is not appreciable and can be neglected if an excess of the sulphuric acid is avoided. If too much sulphuric acid is used low values will be obtained, and for exact analyses it is recommended that a correction be applied. Ten cubic centimeters of 96 per cent sulphuric acid dissolves 0.35 cc. of NO ; 90 per cent acid dissolves 0.2 cc., according to Berl, *Chemische-technische Untersuchungsmethoden*, volume 1, page 160.

The calculation is according to the following formula, which gives the HNO_3 content of the mixed acid tested directly in percentage:

$$\text{Per cent HNO}_3 = \frac{c b v}{(273 + t) \cdot a}, \text{ where } b \text{ is the barometric height, } v \text{ the observed gas volume, } t \text{ the temperature and } a \text{ the weight of the acid sample.}$$

c is the constant for HNO_3 in the measurement of dry NO , and is equal to $\frac{1.3402 \times 30.01 \times 273}{63.02 \times 760} = 0.1011$ (log = 0.00478), where 1.3402 is the weight of a liter of NO at 0°C . and 760 mm., in grams, 30.01 the molecular weight of NO , 63.02 the molecular weight of HNO_3 , the gases being reduced to 0°C . and 760 mm. pressure.

According to Lunge 1 cc. of reduced NO corresponds to 2.8144 mgm. of HNO_3 .

After the determination the gas is allowed to escape, together with the sulphuric acid and mercury salts, and the mercury washed several times with water and finally with concentrated sulphuric acid.

In order to avoid the somewhat troublesome adjustment of the gas, which cannot be accomplished by a simple leveling of the liquids because of the great differences in weight of mercury and sulphuric acid, and also because at times the meniscus does not become sharp promptly on account of bubbles, many prefer to transfer the gas through the three-way stopcock *g* and the bent tube *h* into a second eudiometer filled with mercury, where it can be read off immediately after leveling the mercury in the two tubes.

The nitrometer stands on a low table, protected from air currents and direct sunlight. The table has lateral and longitudinal channels leading to a hole and a receiver, in order to collect easily any mercury which might be spilled.

The nitrometer method is characterized by simplicity, speed and a high accuracy. The time required for an analysis is less than one-half an hour.

The limit of error, with some little practice, is below 0.1 per cent HNO_3 . The loss of nitric acid by evaporation and fuming during charging is very small and does not come into consideration.

3. *Evaporation method.* The evaporation method, in which the nitric acid loss by evaporation does not come into consideration because the nitric acid is determined by difference, takes considerably longer, about two hours, but is just as exact and gives values agreeing well with the nitrometer method. Just as with the latter, the total acidity of a sample is titrated and calculated as H_2SO_4 , while a second sample is fumed off in a platinum dish on a water bath until all the nitric acid is driven off. Water is then added, care being taken to avoid spattering, and it is again evaporated in order to be sure that all the nitric acid is removed. Then the remaining sulphuric acid is titrated and the difference calculated to HNO_3 . Therefore, in this case the sulphuric acid is determined directly and the nitric acid indirectly, while in the nitrometer method the reverse is true. With mixed acids both methods are of equal value. With nitroglycerine spent acids, on the other hand, only the evaporation method gives the true acidity, the nitrometer method including the still dissolved nitric esters of glycerine as the corresponding nitric acid is set free by saponification with the excess of sulphuric acid.

Practically, in the analysis of spent acids, this is of very little importance, since in the denitration the dissolved glycerine nitrates are split up, and the nitric acid derived from them is recovered as weak acid, together with the free nitric acid.

CHAPTER IV

NITRATION

The commercial manufacture of nitroglycerine, particularly the nitration and separation of the acid nitroglycerine from the spent acid, has always been considered one of the most dangerous operations in chemical technique, and properly so. To master this danger requires the greatest care and conscientiousness, first in the choice of the most important raw material, glycerine, and secondly in the most painstaking control of apparatus and adherence to regulations. Only the best trained, reliable personnel should be employed in this operation, and the function of the so-called oil superintendent involves high requirements and experience, care and conscientiousness. Through high standing of the glycerine plants and degree of purity of the product turned out, as well as through construction of the apparatus in as perfect a manner as possible, to-day the operating danger has been reduced to a minimum, and the safety of operation raised to a high standard, so that explosions in nitroglycerine plants occur only seldom.

After a short historical review of the older processes and apparatus the following description will deal with this manufacture as practiced in general at present in most of the large plants.

OLDER PROCESSES

Since at first the requirements were small no one risked the nitration of large quantities of glycerine at one time, and at first worked with the most primitive means designed to produce the product at the point of consumption shortly before use. At this time nitroglycerine was used in a liquid state. According to Guttman nitroglycerine was made for many years in the Vogesen stone quarries at Zabern by the so-called Kepp process, which did not differ appreciably from the method described above for the production of small quantities of nitroglycerine for laboratory purposes except in being even more primitive. The apparatus consisted of merely a stoneware jug for cooling and washing, a cast iron vessel for mixing, a measuring

vessel of lead or porcelain for the glycerine, an iron rod for stirring and a glass filter with a rubber hose and cock for separating the oil from the wash-waters and dropping into glass flasks. At that time 350 grams of glycerine were gradually added to 2.8 kg. of nitrating acid while being stirred. The mixing vessel stood in the jug of ice water, into which the charge was then dumped. The acid water was poured off the separated oil, the latter given several washes or stirrings, and the water decanted. Finally the superficially washed nitroglycerine was separated from the rest of the water in the funnel. In this way about 700 grams, or 200 per cent of nitroglycerine was obtained, and the operation repeated three or four times per hour. Naturally the nitroglycerine could not be pure and was not fit to be stored for a long time.

This method of nitrating in pots was also used in the continental plants even in the seventies. A row of porcelain jugs, or even enameled cast iron or soldered lead vessels, stood in a long trough filled with cold water. Above each mixing vessel there was a corresponding small glycerine vessel provided with a stopcock. The operator held a thermometer in one hand, and in the other a glass rod for stirring. If the temperature rose too high and decomposition commenced, he quickly plunged the jug into the water. In such a case the required personnel was naturally rather large as compared to production. In order to reduce this mechanical stirring was introduced after a time, and a single agitating device used for a row of jugs. A wooden rod, extending above all the jugs, carried a vertical iron rod for each jug, this iron rod being connected to the front wall of the water trough by an eccentric. The forward and backward motion of the latter caused a circular motion of the iron rod in the mixture. The agitating devices were perfected, and assumed many forms. Also the size of the charge increased with increasing requirements of dynamite, the nitrators becoming larger, and gradually taking the form of the cylindrical lead vessels solely used to-day¹ [in Europe²].

A series of ingenious and more or less practical forms of nitrators followed in the course of time, as well as in nitrating processes, but today they have only historical interest and no complete description

¹ Sheet steel nitrators are in exclusive use in the United States.—TRANSLATOR.

² Recent note by the author.

of them can be given here. Gutmann describes them at length, in his *Industrie der Explosivstoffe*, pages 398–405, and they are therefore omitted here. An improvement which is in wide use today was introduced in 1868 by Mowbray in Massachusetts, namely, agitation of the nitrating mixture by compressed air. At many places air and mechanical agitation were used simultaneously, until finally the latter was almost completely given up.³

THE BOUTMY-FAUCHER NITRATING PROCESS

The nitrating process of the two Frenchmen, Boutmy and Faucher, which was used in the French government plant at Vonges for several years until 1882, and also to a considerable extent for a long time in England, deserves mention. It avoids the danger involved in the strong heat of reaction of the nitration, or which was present at that time in the then state of the art, by resolving the process into several steps, based upon the principle expressed by Berthelot in his book *Sur la force des matières explosives* as:

If a system of simple or compound bodies under constant volume or pressure undergoes a chemical or a physical change, without an external mechanical effect being produced, the heat developed is merely dependent upon the initial and final state of the system, and is the same no matter what the kind and sequence of the changes may be.

Accordingly, Boutmy and Faucher distributed the quantity of heat set free during the nitration into two phases, by first mixing glycerine with sulphuric acid to form glycerine sulphate with development of heat, and into this mixture pouring a mixture of nitric and sulphuric acids. In each of the partial process the heating is relatively moderate.

The far stronger and preponderating disengagement of heat occurs in the safe operation of mixing glycerine with sulphuric acid. However, this stage must be well cooled and a relatively low temperature, 40°C., maintained in order to avoid the formation of acrolein and carbonization of the glycerine, which would prevent the separation of the nitroglycerine. The mixing is done in a cast iron trough, with a cooling jacket and stirrer and the glycerine sulphate allowed to cool completely over night in cooled porcelain jugs. Nitration is

³ Agitation by mechanically driven paddles has been used exclusively in the United States for more than fifteen years.—TRANSLATOR.

done in porcelain jugs standing in a cooling bath, the mixture of nitric and sulphuric acids being added gradually while stirring with air, and only a slight rise of temperature is encountered. The mixture is allowed to stand over night, and the acid and nitroglycerine are drawn off by a stopcock in the bottom of the jug.

One hundred parts of glycerine and 320 parts of sulphuric acid are mixed, and a mixture of 280 parts of nitric acid and 280 parts of sulphuric acid is added. There is obtained 200 to 205 parts of nitroglycerine from 100 parts of glycerine. The process was introduced on a large scale in Pembrey, Wales, where 680 kg. of nitroglycerine were made in one operation in a single large nitrator.⁴ The disadvantage of this process, which far overbalances the advantage of low heat evolution in the actual nitration, is the slow separation of the nitroglycerine,⁵ with the resulting long time required and the long time of contact of the nitroglycerine with the acids. Here a spontaneous saponification can be started, favored by the action of the heat developed, and can lead to violent decomposition or even explosion. This action is favored if on mixing the glycerine and sulphuric acid the temperature rises too high and the strongly dehydrating sulphuric acid causes a carbonization of the glycerine. In Vonges, as well as in Pembrey, there were several explosions, and the process was finally abandoned. It is not in use today.

RECENT APPARATUS AND PROCESSES

Lead as a material of construction

Today nitration is carried out almost entirely in cylindrical, autogenously welded lead vessels.⁶ In the manufacture of nitroglycerine the use of iron is avoided insofar as possible, since in case of explosion it forms dangerous missiles, while lead apparatus and accessories, on account of their softness and toughness, are for the greater part found at the center of the explosion as a crumpled mass and are less readily torn into far-flying missiles. In America, where the official supervision is less strict, nitration is carried out in iron apparatus. In Germany this would not be permitted by the authori-

⁴ Guttman, *Die Industrie der Explosivstoffe*, p. 416.

⁵ At that time the undeveloped state of the art of glycerine manufacture retarded the separation considerably.

⁶ See previous footnote on American practice.—TRANSLATOR.

ties. The general use of lead as material of construction also has other advantages. It is comparatively slowly attacked by the acids, and the lead sulphate formed has no harmful effect upon the nitrating process or the nitroglycerine. On the contrary, it acts as clinging, protective coating on the metal walls, protecting them from further corrosion, but this is a slight disadvantage in hindering the transfer of heat. Cooling coils heavily covered with lead sulphate cool poorly and increase the time of nitration because the cooling water is then less efficient. The coating of lead sulphate finally peels off and the attack on the lead is repeated. The softness of the lead also reduces the danger of a metal-to-metal shock causing an explosion of nitroglycerine in the work rooms. This is a further reason for avoiding the use of iron and iron articles in nitroglycerine rooms insofar as feasible.

Nitrators

The cylinder consists of heavy (10 mm.) sheet lead, and should have a height about one and one-half times the diameter. With too wide cylinders a thorough mixing of the contents by the rising compressed air is more difficult and the acids can become stagnant near the walls. The lead cylinder has a lead cover with several windows inserted, affording a good view of the reactions within. If these windows are not used the vapor exhaust pipe can be provided with a lantern in order to be able to note the color of the vapors. However, the first device is recommended. The cover has openings for glycerine and acid inlet pipes, vapor exhaust pipe, thermometer, cooling coil inlet and outlet and compressed air inlet. It can be raised, but is usually cemented down or fastened with a plastic putty. The bottom of the nitrator is somewhat inclined and provided with a large-bore stopcock, cemented in place, so that the products of the nitration can flow out rapidly. The apparatus can stand in a wooden tub in which the cooling water circulates, or it can have double walls. However, with sufficient coil cooling external cooling is superfluous and is not generally used today. Double or triple cooling coils of lead pipe⁷ in concentric form have outlets at the top. The lead pipes can also enter through the walls, and have the outlets below, but this is less customary. Soldering or welding is avoided insofar as possible, as

⁷ Seamless steel coils are used in the United States.—TRANSLATOR.

experience has shown that such joints are most subject to attack by acids. Moreover, the cooling coils have a shorter life than the rest of the apparatus, and if their inlets and outlets are above the walls and not welded to the latter they can be replaced after a period, while any weld which can come in contact with nitroglycerine is naturally out of the question.

The compressed air is led in by a light lead pipe, which distributes the compressed air into the apparatus a short distance above the bottom in various ways, either through a funnel, perforated rings or by blowing against a lead sphere, but always through comparatively narrow openings.

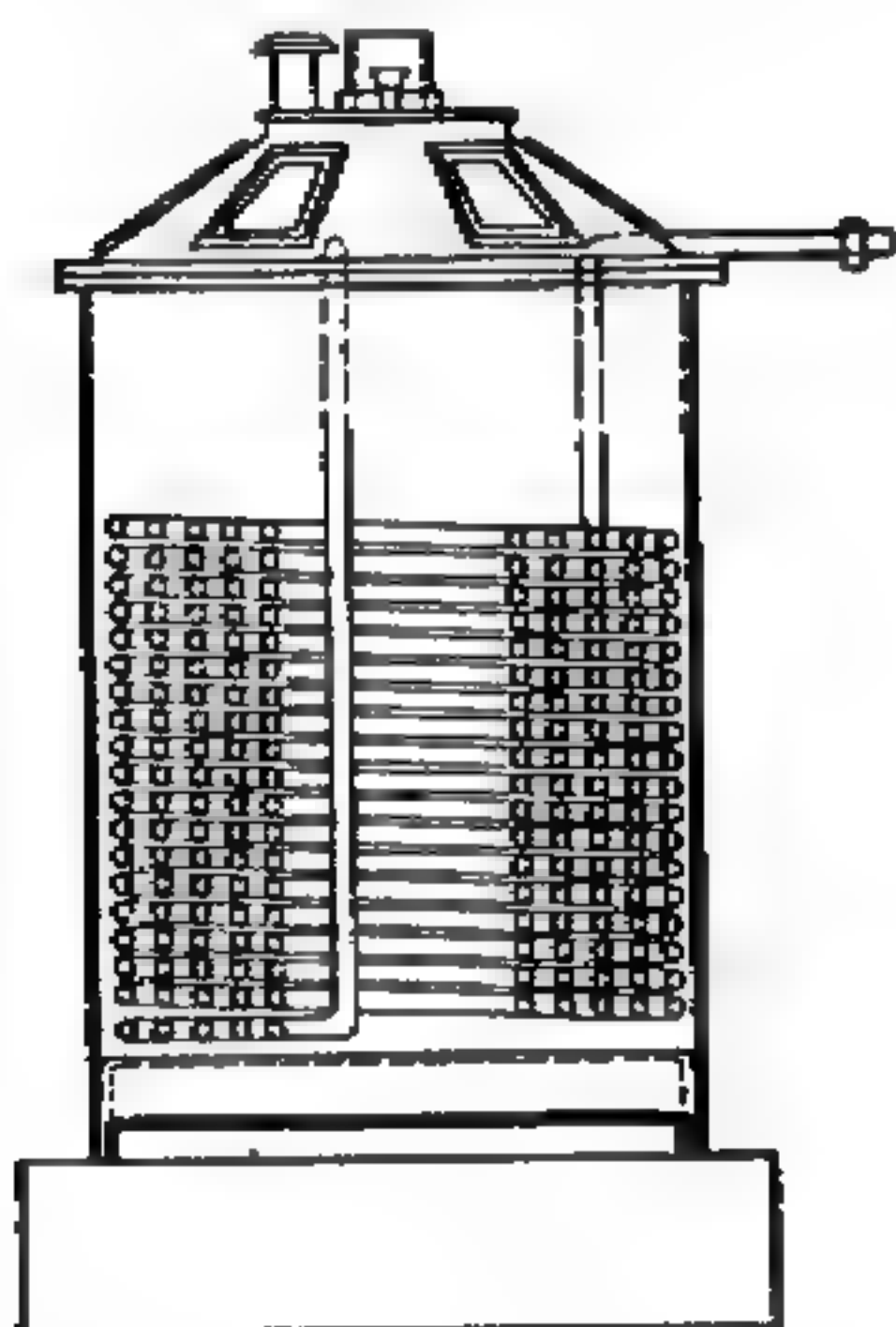


FIG. 6. NITRATOR (SECTION)

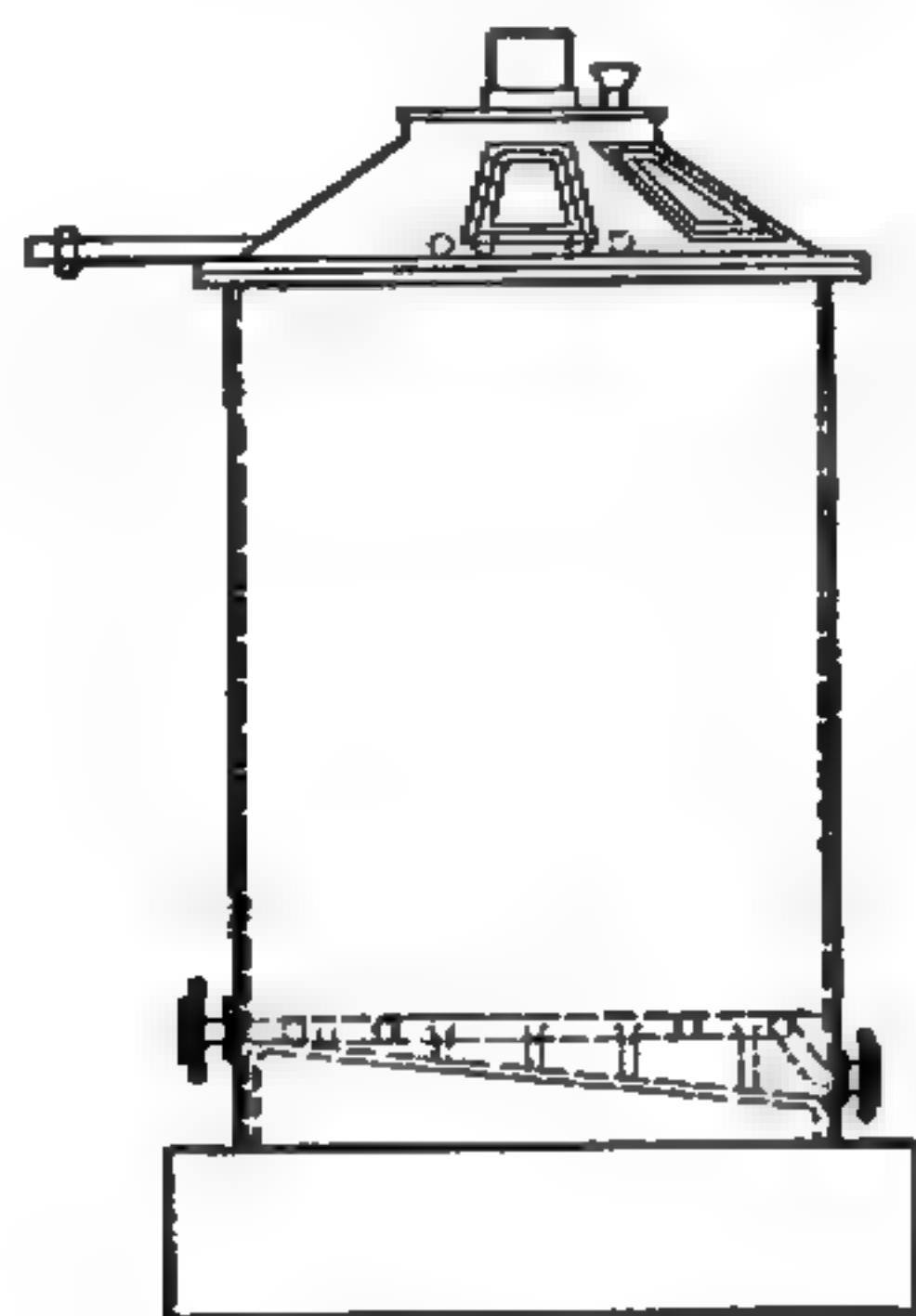


FIG. 7. NITRATOR (EXTERIOR)

It is best to have one pipe leading to the foot of the outlet cock to render agitation possible at this point. Two thermometers project deeply into the liquid, at different depths, in order to be able to note the temperature in both upper and lower parts. The nitrator stands on a wooden platform, and a raised step is necessary for the operator. Figure 6 is a section of the nitrator, and figure 7 an external view.

Nitration

Outside the barricade there are adjacent acid and glycerine sheds. From the acid tank the acid flows into a room where it is weighed or measured, and from here into the nitrator by gravity or a pressure

tank, according to the contour of the ground. The glycerine tank is in a heated shed provided with steam coils, in order to impart to the glycerine the degree of fluidity necessary for rapid and fine subdivision. If the pipe to the nitrator house is long it is best to insulate it suitably and prevent too rapid cooling. The glycerine is measured, or better weighed, and flows through a screen, to remove any foreign substances, into a pressure tank or direct into a container having a sight-glass, from which it flows into the acid or is injected into the acid by compressed air. The injector is placed above the nitrator. In the latter case the injection can also be done directly from the pressure tank. Since in case of explosion it forms a heavy missile the glycerine container is best left outside the nitrator house, and placed behind the barricade.

a. Addition of glycerine. The method of feeding the glycerine into the acid mixture has received a great deal of attention in the past. It is very important to obtain the highest possible velocity of subdivision in order to avoid local overheating, which can be accompanied by danger of decomposition, even though merely local, and also reduction of yield. For this reason various distributors have been made which permit the glycerine to flow out on the surface of the acid in many fine streams. Recent experience has shown that even on a very large scale the glycerine can be allowed to flow into the middle of the acid surface in a stream about as thick as the finger without danger provided that the acid mixture is properly agitated. The best temperature of the glycerine is 30 to 40°C. Appreciable differences in temperatures have no noticeable effect on nitrating time and yields. As previously stated, the glycerine can also be fed in under pressure. The rate of addition of glycerine is regulated by a valve, preferably maintained in a closed condition by a spring when not in use and requiring considerable pressure by the hand to keep open. When the hand is removed it closes automatically. If the operator happens to leave the nitrator on account of some danger the glycerine is automatically cut off. The glycerine distributor is attached to the glycerine pipe by a rubber hose so arranged that after all the glycerine has been added it can be removed. This prevents any drops of glycerine from falling to the bottom of the nitrator after the charge has been run out, mixing with the acid residues on the bottom and forming nitroglycerine which could decompose suddenly from lack of agitation and cooling. Such cases have been known,

where the glass windows of the nitrator were broken. Although the danger is comparatively small, any possibility of decomposition must be carefully avoided on account of the ease of propagation of the explosion to adjacent small quantities of nitroglycerine. Injectors have been made of stoneware, porcelain or of metal carefully covered with lead, which when placed beneath the surface in the lower part of the nitrator feed the glycerine into the acids under pressure by compressed air. The distribution is rapid and thorough, with vigorous agitation, yet these injectors require frequent repairs, and the point where they enter the nitrator is a source of anxiety.⁸

b. Preparation. After making all preparations, particularly the testing of the safety devices to be described later, and coating all the earthenware cocks with paraffin oil, the nitrating acid is allowed to flow into the nitrator, which is filled one-half or at most two-thirds full to cover the cooling coils. The cooling water⁹ is turned on to the coils, and the addition of glycerine commenced as soon as the acid has become sufficiently cooled (below 20°C.) and is being sufficiently agitated by control of the compressed air valve.

c. Agitation by compressed air. The compressed air comes from a compressed air tank, called an "oil separator," outside the barricade, which serves to remove the particles of machine oil in the pipe from the compressor and also to separate the water from the compressed air. It also maintains the pressure constant during the operation. The compressed air is usually at 4 atmospheres, because a pressure as high as this is often required to transport the acid in these plants to different elevations. Such a pressure is by no means necessary for agitation in the nitrator, but large apparatus requires considerable pressure to overcome the hydrostatic pressure of the dense acid mixture and to keep it in vigorous agitation.

The previously customary mechanical agitation has been abandoned to-day except in a few cases, as in America. The only disadvantage of air agitation is that during the nitration an appreciable quantity of nitric acid is driven off by the compressed air and carried away with it, and thus removed from the reaction. The fumes are drawn off through a vent pipe by an exhauster, thus preventing

⁸ This is avoided by the use of mechanically driven paddles.—TRANSLATOR.

⁹ Calcium chloride brine at -23 to -18°C. is almost universally used in the United States. When circulated within steel cooling coils this gives a good heat transfer and rapid cooling.—TRANSLATOR.

the acid vapors from escaping into the open room from leaks in the nitrator cover. Since these acid vapors damage the surroundings and vegetation they are condensed by a plate tower or similar device. Because an excess of water is required for this condensation only dilute nitric acid is recovered. Too violent agitation and removal of the nitric acid can affect the yields. Laboratory tests in small experimental installations show that under uniform conditions a normal air agitation gives 1 to 2 per cent lower nitroglycerine yield than mechanical stirring. If for any reason, such as a defect in the compressor, the compressed air suddenly fails, the addition of glycerine is immediately stopped and the nitration finished by the use of carbon dioxide in place of compressed air, the former being contained as a liquid in a pressure bottle always attached to the air pipes. Compressed nitrogen is better.

d. Nitrating temperature. The addition of glycerine is so regulated that the temperature of the mixture does not exceed a certain limit. If it is desired to complete the nitration within a given time, this time is dependent upon the temperature of the cooling water, the size of the cooling surfaces and the velocity of circulation of the cooling water. However, it is never permissible to exceed a temperature of 30°C. If, as in hot countries, insufficient cold cooling water is available, or water above 20°C., the time of nitration is extended correspondingly, and the size of the cooling surfaces is made as large as possible, the water reservoir cooled by ice, or use made of artificial refrigeration with very cold brine. Nitration at higher temperatures, even above 40°C., is indeed possible, especially with anhydrous mixed acids, and has even been practiced on a small scale. However, for various reasons it is not to be recommended and would be dangerous on a factory scale. The yields of nitroglycerine fall with rising temperatures, as will be shown later under "Operating Results," and above 30°C. this becomes appreciable. In addition to the esterification there is always a limited amount of oxidation taking place, which increases with rising temperatures. Furthermore, the temperatures shown by the thermometer point to the possibility of local heat centers in the nitrating mixtures of appreciably higher temperatures, so that with too high average temperatures it must be expected that at any possible stagnant point a sudden but transient oxidation can occur, which can lead to a violent decomposition, usually ending in an explosion of the entire charge. In many plants a temperature of 25°C. is not exceeded. With very cold ground or

well water, or with very cold river water in winter it is not any particular trouble to maintain 20°C. The constantly rising price of glycerine in recent times has made even slight improvements in yield profitable. It has been found economical to provide large nitroglycerine plants with artificial refrigeration, so that brine cooled to about -10°C. can be circulated through the cooling coils instead of water. It then becomes possible to nitrate at about 12°C. with an improvement in yields of about 3 to 4 per cent. Lower temperatures cannot be used, because otherwise there would be the possibility of the nitroglycerine freezing, which would cause undesirable complications.¹⁰

e. Time of nitration. The time taken by a nitration depends naturally upon the size of the cooling surfaces and the temperature of the cooling water. As a rule it also increases somewhat with the size of the charge. The usual apparatus allows a charge of 100 kg. of glycerine to be nitrated at 30°C. in about twenty minutes with a water temperature of 10 to 12°C. Moreover, the initial temperature of the mixed acid is not without effect, so that in winter the time of nitration is somewhat shorter on account of the acids being stored in the open in cold places.¹¹

Size of the charge

The size of the charge varies widely according to requirements. The normal charge is 150 to 250 kg. of glycerine for most German plants.¹² In Modderfontein, Transvaal, 400 kg. of glycerine is nitrated with about 2600 kg. of mixed acid and about 900 kg. of nitroglycerine produced in one operation. In some American plants as much as 450 kg. of glycerine are nitrated at once. Even here the time taken by the operation is little more than half an hour.

Decomposition; safety devices; safety (drowning) tank

In former times decompositions and even explosions in nitration were frequent. To-day these, especially considering the amount

¹⁰ With the almost universal use of diglycerine mixtures, lower temperatures of nitration, with correspondingly better yields, can be employed, such as 5 to 7°C. being usual in the United States.—TRANSLATOR.

¹¹ Particularly true in States along the Canadian border, where -30°F. is encountered.—TRANSLATOR.

¹² 500 kg. is usual in the United States, requiring about fifty minutes.—TRANSLATOR.

produced, are very rare and can only be explained by gross carelessness or poor materials. Impure glycerine, formerly a frequent cause of decompositions, can hardly ever occur now because the technique of glycerine distillation has reached a high plane. Formerly decompositions were possible as a result of leaks in the apparatus, particularly in the cooling coils, thus allowing water to enter the charge and heat it suddenly. For this reason nitrators and cooling coils are tested at least once a day for leaks, and the nitrator allowed to stand over night under water pressure with the bottom outlet closed so that in the morning a defective spot will be revealed by the water which has collected. It is also important for the safety of the operation to have the water circulation so arranged that the water in the cooling coils within the nitrator is under suction. Aside from the insertion of an intermediate reservoir to prevent the total water pressure exerting any high pressure upon the cooling coils, suction can easily be arranged in a hilly location by using a syphon outlet as long as possible and having its outlet under water. If its diameter is greater than that of the cooling coils even a considerable positive pressure of the cooling water above the nitrator can be equalized or converted into a suction. With the aid of a small brass valve on the inlet and outlet of the coils it can be told whether there is pressure or suction in them. By a stopcock in the outlet beneath the apparatus it becomes possible in all cases to hold water pressure in the coils during any pause in the operation to test for leaks, for example over night.

In spite of all these precautions it is advisable to change the coils as well as the entire nitrator after a certain number of runs, without regard to its apparent condition. The cost of doing this is not high as compared to the increased safety.

The operators are required to watch constantly the glycerine feed, the thermometer, the agitation of the mixture and the color of the escaping vapors. Should the temperature rise unduly in spite of careful operation the glycerine is shut off and all air valves opened wide. If the temperature still rises in spite of this, or if a decomposition starts, as evidenced by the deep red color of the vapors, the operator must quickly open the exit cock leading to the safety (drowning) tank and leave the building.

Safety (drowning) tank. For such cases a so-called safety (drowning) tank is provided, either beneath the apparatus in the lower part

of the nitrator house, or outside of it. Such a tank may be a pit of cement or masonry, or a wooden tank lined with sheet lead. Since in case of need the diluted acids never remain in it long, mere wooden tanks are sufficient. The tank should be large enough so that when it is half filled with water the amount of water is four to five times the quantity of the acid to be diluted. The bottom is somewhat inclined, and at the lowest part there is a stoneware stopcock to allow the accumulated nitroglycerine to be drawn off. Air agitation, water inlet and overflow are provided, to give proper mixing and change of water at the spot. The water is renewed from time to time to avoid any possible vegetable growth. Moreover, the air agitation is tested by turning it on occasionally. If, as is usual at many places, the tank serves as a drain for the wash-waters from the nitrator and separating funnel, it is cleaned of lead mud every month to prevent the air holes in the agitator from becoming stopped up just when needed, as may otherwise happen, and allow the heavy, concentrated acids to remain unmixed with the water at the bottom and finally cause a saponification of the nitroglycerine from lack of water due to lack of agitation, which in such a case can lead to an explosion of the nitroglycerine under the water in the drowning tank.

This drowning tank should be used only in case of actual danger. Drowning of the charge is accompanied by the development of large quantities of nitrous acid vapors, which injure the nitrator building, and the removal of the nitroglycerine from the tank is difficult and inconvenient. This led Guttman to the conclusion that the drowning tank would be better if outside the building. The thin film of the decomposing mass in the long pipe which would then be necessary would diminish the danger. To this it can be countered that this device is to be preferred in case the charge is dropped down on account of danger in the vicinity, but in case a suddenly decomposing charge is encountered the resistance of a longer pipe only retards the drowning, and even a wide, rapid outlet does not exclude an explosion in the pipe itself. The drowning tank affords only a limited protection in the case of sudden decompositions. It has sometimes happened that before the charge had entirely run out into the drowning tank, which requires from one and one-half to two minutes on account of the large quantity involved, the remainder in the nitrator exploded. The device gives very good service in case of danger in adjacent buildings. With an explosion in the vicinity, with

threatened injury to the lightly constructed nitrator house, the danger from the nitroglycerine present is greatly reduced if the concentrated acids are drowned and the nitroglycerine itself is under water.

Automatic drowning of the charge; danger signal. In order to be not too dependent upon the presence of mind of the operator in case of sudden danger, and to be able to empty the charge without the delay necessary for turning a convenient handle or even during flight from the building, an ingenious device has been provided and used in most plants. In addition to the outlet cocks on the nitrator and separator (see "Separation"), cylinders are used in which a piston is moved by air pressure. The piston is connected to the stopcock by a lever and chain. All these air pressure cylinders of a nitroglycerine plant are connected to the same compressed air pipe, from

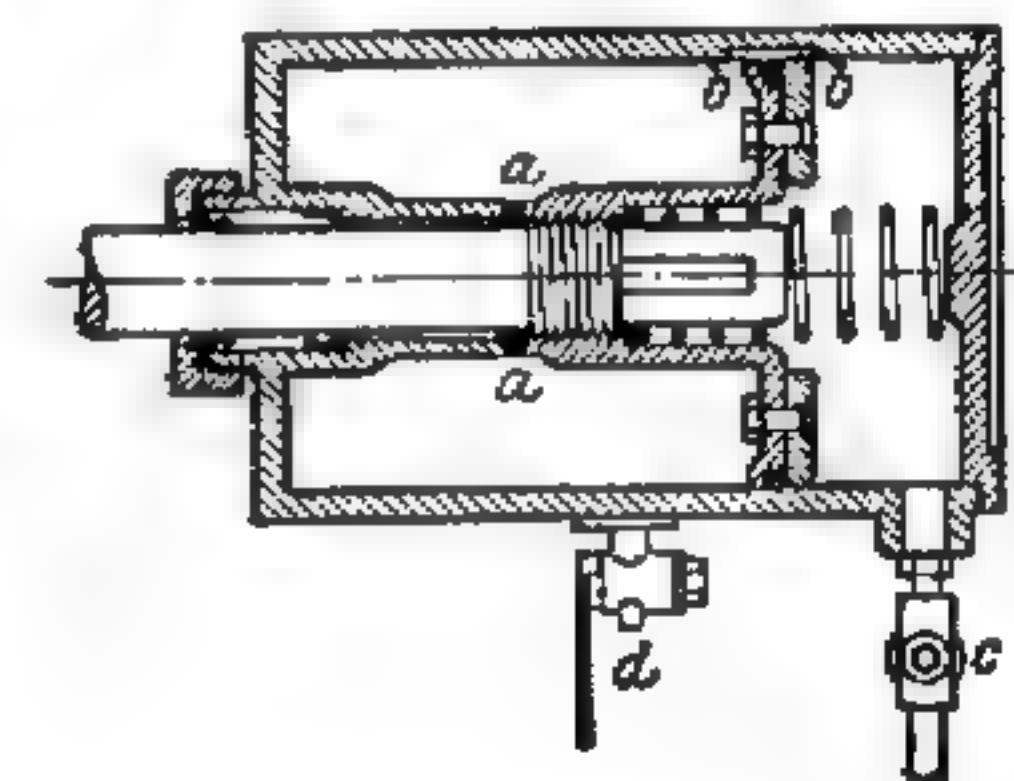


FIG. 8. AUTOMATIC COMPRESSED AIR VALVE

which branches lead to the nitrator and drowning tank. When air is turned on to these pipes, as can be done from several suitable points by an easily operated valve, the cocks of all the nitrators and separators immediately open and the acid charges fall into the drowning tanks, in which they are agitated by compressed air. This air pipe passes through all the rooms in the danger area and on each branch carries a signal whistle to inform everyone of the threatening danger in an adjacent room, so that they can hurry through the tunnels through the earth barricades to the outside of the wall. The air pipe also passes through the shelters in the barricade, so that the safety device can also be operated from here in case the operator has omitted this in his hurried flight.

Lessor, government and commercial councilor, considers this device capable of being improved, since even with the most careful placing of the

air pipes under ground they can be injured by an explosion in one of the buildings, for example the mixing room, so that they become inoperable.¹¹ He therefore considers it better to maintain the cylinder constantly under pressure, so that the piston will move as soon as the pipe is opened or broken. In the latter case the action is automatic. In order to be able to give the necessary alarm signal in all the rooms it would be necessary to have a second hand valve on a special air pipe. The device is readily understood by reference to figure 8. A spiral spring presses the piston to the left against the packing ring *a*. The compressed air enters at *c* and through the fine slits *bb* behind the piston also. If the compressed air pipe is broken, or if an air valve on it at any point is opened, the right side of the cylinder is opened, and from the left side of the cylinder the compressed air is unable to escape rapidly and pushes the piston to the right, so that the packing is then taken care of by the rings. To reset it, the left side is emptied by the valve *d*. With this device two pipes are necessary, because the air for stirring the nitrator must come from a special pipe.

In case of failure of the air agitation from a defect in the pipes or the compressor a large compressed air tank is provided in the vicinity of the nitrator and wash-house, which will last a certain time at least, and on the other hand flasks of liquid carbon dioxide are placed at suitable points in the nitrator house and beneath it. The use of the latter seems somewhat a question because when their valves are opened rapidly, as in case of danger, they freeze easily. Lessor therefore recommends compressed nitrogen in place of carbon dioxide.

Every day, before beginning the operations of filling the nitrator, the safety devices are tested for smooth operation. Often it is a regulation that the work for the day shall not be started until the supervising chemist has personally tested them.

Completion of nitration; letting down the charge

When all the glycerine has been added the glycerine valve is shut off, the rate of stirring cut down and stirring continued for a few minutes in order to be sure that the mixture is homogeneous in all parts of the nitrator. Then the chain of the safety device is removed from the stopcock, the nitrator connected to the separator either by a knee-shaped, wide lead pipe or by a solid connection by a valve of corresponding size, and while continuing to stir gently the charge is run down into the separator, which requires from one and one-half to two minutes.

¹¹ *Z. Schiess- u. Sprengstoffw.*, 1907, p. 48.

Supplement: Patent literature on nitration. German patents 6208 (1878) to Kurtz, for the introduction of glycerine beneath the acid by a distributor, with air agitation and continual drawing off of the nitroglycerine, and supplement 8463 for making an emulsion of glycerine by air. Continuous nitration is unattainable in practice. 11141 (1880) to Engels for a portable device for the manufacture of nitroglycerine. 17568 (1881) to Schilling for a glycerine distributor. 29130 (1883) to Schröder for apparatus for the manufacture of nitroglycerine by blowing in the glycerine from beneath the surface of the acid, together with the compressed air. 51660 (1889) to Siebert for addition of ammonium nitrate or ammonium sulphate to the nitrating acids (in practice of no effect or purpose). 183183 (1902) to Evers for a process and apparatus for the continuous production of nitroglycerine by mixing the nitrating acid and glycerine by the use of a suitable spray nozzle (not known to have had any practical use). 195231 (1904) to Dynamit A.-G. vorm. Nobel & Co. (or Zentrastelle für wiss.-techn. Untersuchungen, Neubabelsberg) for a process using instead of fresh nitrating acid a portion of the spent acid from the previous operation, revived to the original composition. Comparatively weak acids were used, e.g., 60 per cent H_2SO_4 , 30 per cent HNO_3 , 10 per cent H_2O , in corresponding excess, to render the nitration smoother and less dangerous and so obtain relatively good yields (225 to 226 per cent), because the glycerine sulphate remained in the spent acid and because at the low concentration the unconsumed glycerine in part again entered the next operation. For revivification, however, high strength oleum was necessary, and it was preferable to use oleum at the start to produce a highly concentrated nitrating acid and so obtain better results. For this reason the patented process has found no practical application.

British patents 1813 (1864) to Alfred Nobel for the manufacture of nitroglycerine and use of same in the explosive art. 1919 (1878) to Huntley and Kessel for the nitration of glycerine with $8\frac{1}{2}$ parts of a mixture of 670 parts of sulphuric acid and 350 parts of sodium nitrate. 7433 (1884), corresponding to German patent 29130, which see. 13907 (1889) to La Compagnie Forcite, for a nitrator having good temperature regulation. 15983 (1901) to Nathan, Thomson and Rintoul, for a nitrator also serving as a separator. 2776 (1905) corresponding to German patent 195231, which see. American patent 913653 covers the same thing.

French patent 366593 (1906) to Nathan, Thomson and Rintoul for the use of fuming sulphuric acid in the manufacture of nitroglycerine.

CHAPTER V

SEPARATION

The nitroglycerine formed is as good as insoluble in the spent acid mixture, which consists of 72 to 74 per cent H_2SO_4 , 9 to 10 per cent HNO_3 and 16 to 18 per cent H_2O , and after the nitration is finished it forms with this spent acid a more or less fine emulsion. On account of the differences in specific gravity the nitroglycerine rises to the surface of the acid after a certain time.

INDIRECT SEPARATION

In the first nitroglycerine plants no value was placed upon the recovery of the acids and the nitroglycerine was separated from them by merely allowing the whole charge to run into a large excess of water, whereupon the heavy nitroglycerine immediately settled to the bottom and the water and acids were separated by decantation. According to Guttman, large, wooden tanks, usually lined with lead, were used for this purpose, often as large as 4 meters in diameter and 2.5 meters high, half filled with water. The mixture was let in slowly while stirring with wooden paddles, or a number of perforated wooden plates fastened to a vertical shaft were moved back and forth. The bottom of the tank was inclined, and at the lowest point there was a stoneware stopcock to draw off the nitroglycerine. On drowing the charge considerable heat was developed, which was controlled by a thermometer to avoid any dangerous rise in temperature. At times the drowing tanks were so arranged that they could also be used for the separation.

In indirect separation all of the spent acid is lost because of the great dilution with water, and the large quantities of strongly acid water go into the ground or streams, which can cause trouble for the plant, depending upon its location. Moreover, considerable quantities of nitrous gases are evolved, which injure the workmen and the vegetation. For reasons of economy as well as hygiene, indirect separation was gradually abandoned, and today is completely given up.

DIRECT SEPARATION

In the manufacture of nitroglycerine on a large scale attempts were made at first to skim off the nitroglycerine floating upon the acids by wooden ladles, but this was troublesome and inconvenient and was given up on account of accidents. Direct separation was not adopted generally until about 1877.

Remarks on the process

With the difference of specific gravity of 1.6 for nitroglycerine and about 1.7 for spent acid the mixture should separate rapidly, and as a matter of fact with very pure raw materials there is a very rapid separation, becoming complete in small laboratory charges with mechanical agitation in a few moments and with large factory scale charges in about ten minutes. However, small amounts of impurities in the glycerine, such as fatty acids or mucilaginous or colloidal substances or finely divided lead sulphate in the acids, hinder rapid separation, aside from the intimate emulsion formation due to the air agitation. With large charges separation as a rule takes twenty to thirty minutes, but under unfavorable conditions it can take much longer. Governing factors of time of separation are, within certain limits, the temperature of the mixture, the shape of the separator, and the size of the charge. In general, large charges require a longer time for separation than small ones. With shallow separators and thin layers a shorter time is required than with deep ones, on account of the shorter path which the slowly moving particles of nitroglycerine have to traverse. The effect of temperature is appreciable. Warm charges separate more quickly than very cold ones because of the reduced internal friction of the former. For this reason, even with artificial cooling and a nitrating temperature of 12 to 15°C., at the end of the nitration the temperature is preferably allowed to rise to 18 to 20°C., so as not to make the separation too difficult. However, the effect of this factor is comparatively small as compared to the retarding influence of the first-mentioned impurities in the glycerine or suspended in the acids. This delay with turbid acids, poorly separating nitroglycerine, or both, has often seriously limited the output of a plant, and in stormy years or in times of frequent storms has caused much trouble because in storms the manufacture of nitroglycerine ceases and the operators go to places

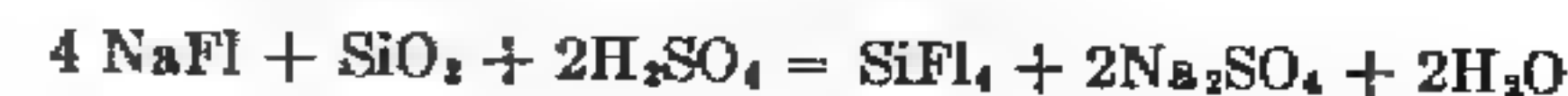
of safety, but on the other hand it is not allowable to leave a charge in the process of separation without supervision. For this reason much study has been given to separation, and attempts have been made to shorten artificially the time taken in separation. This was first accomplished by a process invented by the author, patented in 1904¹ by the Dynamit A.-G., in which small quantities, e.g., 0.5 to 2 parts per 1000 parts of glycerine, of aliphatic hydrocarbons like paraffin, vaseline, paraffin oil, or high-molecular fatty acids like stearic acid, were finely subdivided either in the glycerine or in the acids toward the end of the nitration, which by a true surface effect favored the separation of the emulsion and facilitated the rise of the drops of the nitroglycerine through the acids. A requirement of effectiveness is that such added compounds shall not be soluble in either the glycerine or the acids and shall be unchanged by the latter. This requirement is met by the paraffin hydrocarbons at the temperatures in question. Moreover, commercial paraffin oil or vaseline contains some aromatic hydrocarbons. These are nitrated, and because of the small amount present they dissolve in the acids completely. The preponderating amount of the undissolved aliphatic portion arises with the nitroglycerine and is later washed away when the latter undergoes the washing treatment. This process has been used ever since by the Krümmel dynamite plant, for example, where the small amount of 100 cc. of paraffin oil is added to a charge of 250 kg. of glycerine and about 1600 kg. of mixed acid, and the time of separation reduced from the normal time of thirty to forty minutes to fifteen to twenty. Usually the main quantity of the nitroglycerine separates after five to ten minutes, so that in case of danger from storms the latter can be run off very rapidly and put under water, but with such a rapid separation there is a somewhat increased after-separation.

A year later, in 1905, the Eastern Dynamite Company, Wilmington, Delaware,² patented another process for the same purpose. According to the claims of this patent glycerine or the acids in many cases contain small quantities of dissolved, colloidal silicates or silicic acid, which retard separation. By addition of a correspondingly small quantity of hydrofluoric acid or a fluoride, e.g., sodium

¹ German patent 171106; British patent 13562, 1904.

² German patent 181489; British patent 20310 19050 United States patent 804817 to Charles Reese.

fluoride, it is claimed that the silicic acid is converted into silicon tetrafluoride and eliminated, and thus the retarding action upon the breaking of the emulsion is avoided. The explanation of the reaction is not at all satisfactory from a chemical standpoint, because it must be assumed that the concentrated acids break up the gelatinous condition of any silicates or silicic acid present by the removal of water, and any traces of amorphous silicic acid could hardly exert any appreciable effect upon the time of separation. The results obtained with this process, which was also frequently used in Germany, were variable and often questionable. The explanation of these conditions was shown sometime later by the process claimed in German patent 283330 (corresponding British patent 14586 of 1921) issued to the Rhein. Dynamitfabrik Köln. It was shown that chemically pure sodium fluoride did not give this reaction, but only the commercial grades of the salt which contained considerable amounts of impurities in the form of silicic acid or silicates. Exact observations by the Opladen plant of the Rhein. Dynamitfabrik Köln showed that the improvement in the separation is no way due to a negative action in destroying the gelatinous silicic acid, but to a positive effect due to the development of gaseous silicon tetrafluoride during the separation. The patented process consists in adding to the charge toward the end of the nitration small quantities of fluoride and silicic acid or salts of hydrofluosilicic acid. The bubbles of silicon tetrafluoride gas, by rising in the separator, favor the separation of the nitroglycerine. In the practical use of the process an intimate mixture of sodium fluoride and kieselguhr is added just before the end of the nitration. If added at the beginning of the nitration no effect is noticed, since the silicon tetrafluoride is thus developed during the nitration and blown out by the compressed air, which is a striking proof of the fact that it is just these gas bubbles which aid the separation. The development of silicon tetrafluoride gas is according to the following equation:



or



In the latter case the excess hydrofluoric acid can be utilized by a corresponding addition, e.g., 10 per cent, of silicic acid, which may be

in the form of kieselguhr. Ten to fifteen grams of sodium fluosilicate, or a mixture of sodium fluoride and kieselguhr corresponding to the above formula, are sufficient for a charge of 100 kg. of glycerine. The action is similar to that of paraffin oil. Both processes are also used simultaneously.

According to German patent 249573, issued to the Westfälisch-Anhaltische Sprengstoff A.-G., Berlin, in 1911, separation of nitroglycerine is also facilitated by the addition of small quantities, e.g. 0.02 to 0.05 per cent, of silicates like kaolin or talc. The reason for the action in this case is not clear. Tests made by the author in this connection gave an opposite effect. Still another process for shortening the time of separation of nitroglycerine is that of the British patent 18597 of 1907 issued to J. F. Lehmann, in which an electric current is passed through the separating charge. The resulting electrolysis causes bubbles of gas, which rise to the surface, and are said to favor the separation of the nitroglycerine. Nothing is known regarding the practical use of this process. Certainly no one would be inclined to increase the danger of the operation by using an electric current.

Apparatus

The separator most frequently used consists of a rectangular vessel of heavy sheet lead, with an inverted, conical bottom (fig. 9). This rests on a strong wooden support, and is covered with a flat or raised cover consisting of a cast iron or lead-covered framework in which glass windows are inserted to afford free observation of the whole surface of the charge. The inlet pipe passes through an opening in the wall of the separator. A fume pipe leads from the center of the cover, into which compressed air is blown to eject the fumes, and a thermometer extends from the cover down into the liquid. Usually there is also a lead pipe reaching to the bottom, through which compressed air can be blown in case irregular, spontaneous heating is encountered. At the base of the conical bottom there is a lantern, so that it can be seen when the cloudy acid gives way to the clear, yellow nitroglycerine as the acid is being drawn off. This lantern is connected to a wide pipe having one or more stopcocks. The device can be so operated that one stopcock is connected to the pipe leading to the after-separator, a second to the pre-wash tank or wash-house, and a third direct to the drowning tank. Frequently, however, there is only one stopcock provided, which by means of a movable, wide, knee-shaped lead pipe can be connected to the three outlets described above. During the separation the stopcock is connected to the

drowning tank and so joined to the safety device, described in the chapter under nitration, that by the operation of the latter the charge flows down into the drowning tank. Frequently there are to the right and left, beneath the separator, long boxes covered with glass windows, into which the above-mentioned knee-shaped lead pipe can be inserted through an opening in the cover. One of these boxes is for acid and another for the nitroglycerine. From these two intermediate boxes pipes lead to the after-separator and to the wash house. It is determined by calculation and experience to what height the acid level will reach after the separation, and where the line of separation between the acid and the oil will be in the course of normal operation.

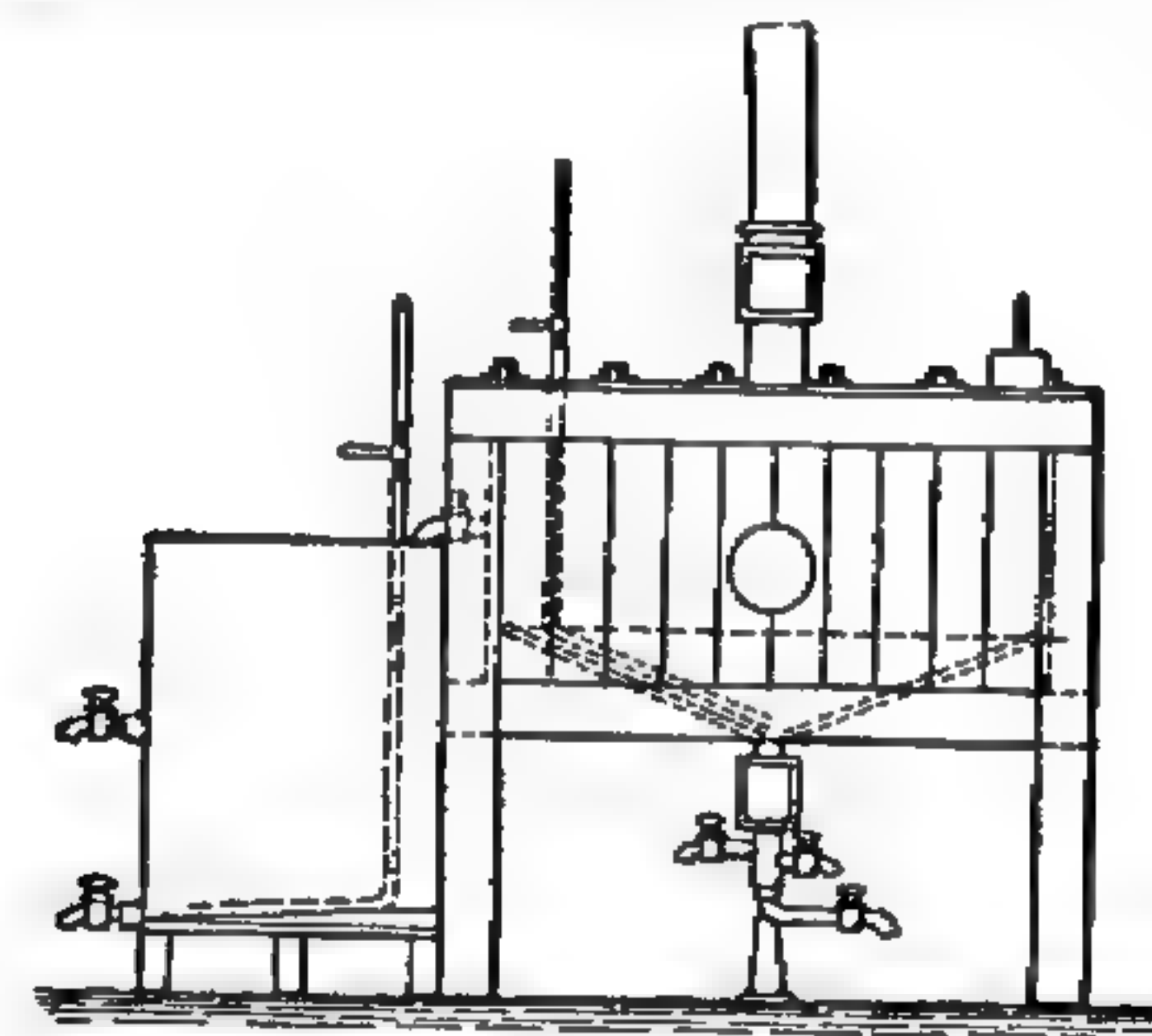


FIG. 9. NITROGLYCERINE SEPARATOR

There is a notch cut in the front wall of the apparatus, and a lead frame welded around it into which a glass window is inserted. This permits of exact observation of the course and end of the separation. At first the nitroglycerine is seen to rise in large, and later in small drops, until the layer of oil reaches the level of the window. The line of separation at first grows like a tree, and then is seen to break and finally form a sharp line. If in the course of minutes the oil layer does not increase noticeably the separation is finished and withdrawal of the acid layer and oil is started. Usually the latter flows to a pre-wash tank, where it is vigorously agitated by compressed air in cold water before it flows to the wash house and stabilizing tank. One of the above-mentioned lead boxes beneath the separator can be used as the pre-wash tank, as it is always filled with water and provided with air agitation.

In many plants a small stopcock is provided at about the height of the line of separation, through which the main quantity of the nitroglycerine is drawn off immediately after it separates and allowed to run into a pre-wash tank near the separator. This has the advantage that the whole quantity of acid nitroglycerine does not stand for a long time over the acid, and in case of any possible heating or local decomposition there is only a small quantity of acid nitroglycerine present. Moreover, the reduction in the thickness of the layer of oil facilitates further rise of drops of oil. After almost all of the oil has been drawn off the acids are allowed to run out through the stopcock at the bottom, the oily residue collected in suitable buckets and added to the pre-wash tank.

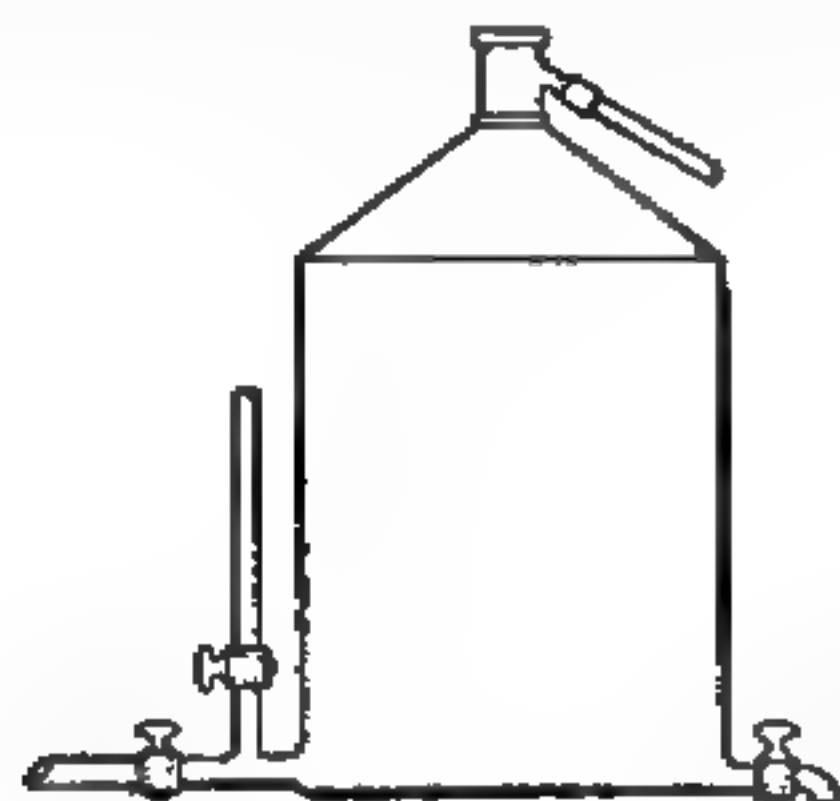


FIG. 10. DISPLACEMENT SEPARATOR

Displacement separator

The advantage of not having to wait for complete separation when drawing off the acid and nitroglycerine, but instead drawing off the acid nitroglycerine as it separates from the spent acids and bringing it under water, has been attained in recent times by another form of separator, shown in figure 10.³ This cylindrical vessel resembles the after-separator tank to be described later, as well as the combined nitrator-separator of Nathan, Thomson and Rintoul, which will also be described further on. The cylinder is made of heavy sheet lead, has a conical cover of the same material, which is joined to a wide lead pipe provided with a lantern from which a bent lead pipe leads off at the side of the pre-wash tank or wash tank. Like the other vessel it is provided with a thermometer. At the bottom there is a lead pipe with a stoneware stopcock leading to the drowing tank

³ This is never used in the United States.—TRANSLATOR.

or after-separator. A branch of this lead pipe leads to an elevated lead tank filled with spent acid, which is controlled by a third stoneware stopcock. When this latter stopcock is open acid of the same composition as that in the separator runs down from the elevated tank into the separator, raises the level of the charge and displaces the separated nitroglycerine through the overflow into the wash tank. At first the separator operator waits a few minutes until a certain quantity of oil has separated clear, and then he gradually displaces all of it as it separates. This can be observed through the lantern. During the time of separation the displaced portion of the nitroglycerine is constantly washed with cold water by air agitation. Thus time is saved and a complete separation by means of a simple, convenient method is attained, and at no time is a large quantity of strongly acid nitroglycerine held for a long period over the acids. It also avoids subjecting a surface of acid nitroglycerine with the impurities from the glycerine floating on it to air for a long period.

Combined nitrator-separator process of Nathan, Thomson and Rintoul

In British patent 159830 (1901), and 3020 (1903) Nathan, Thomson and Rintoul described an apparatus and a process which has been in use since that time in the English government powder plant at Waltham-Abbey. In this process nitration and separation take place in the same apparatus, and the device used at other places for the after-separation is thereby avoided or rendered superfluous in that after the end of the separation and withdrawal of the nitroglycerine a small quantity of water, about 2 per cent, is added to the spent acids while being agitated with air, which is of no importance as regards recovery of the acids but which on the other hand causes a sufficient change in the composition and such a displacement of the relations of the components governing the formation and separation of the nitroglycerine that no subsequent formation and separation of nitroglycerine can occur. The spent acids so treated can be stored at any place, shipped, or sent directly to the denitrator. Figure 11 shows the apparatus in plan and section. It has the external form of the usual nitrator, and combines this with the principle of the separator for the displacement process just described.⁴

The inlet for the nitrating acids is not, as is customary, at the

⁴ This is never used in the United States.—TRANSLATOR.

top, but by way of a pipe connected to the lowest part of the apparatus. This pipe has three branches, one (b) which leads to the denitrator or to the spent acid pressure tank, the second (c) to the drowning tank, and the third (d) extends upward and divides into two branches, one leading to the nitrating acid supply tank, the other to an elevated tank containing spent acid. The acid pipe

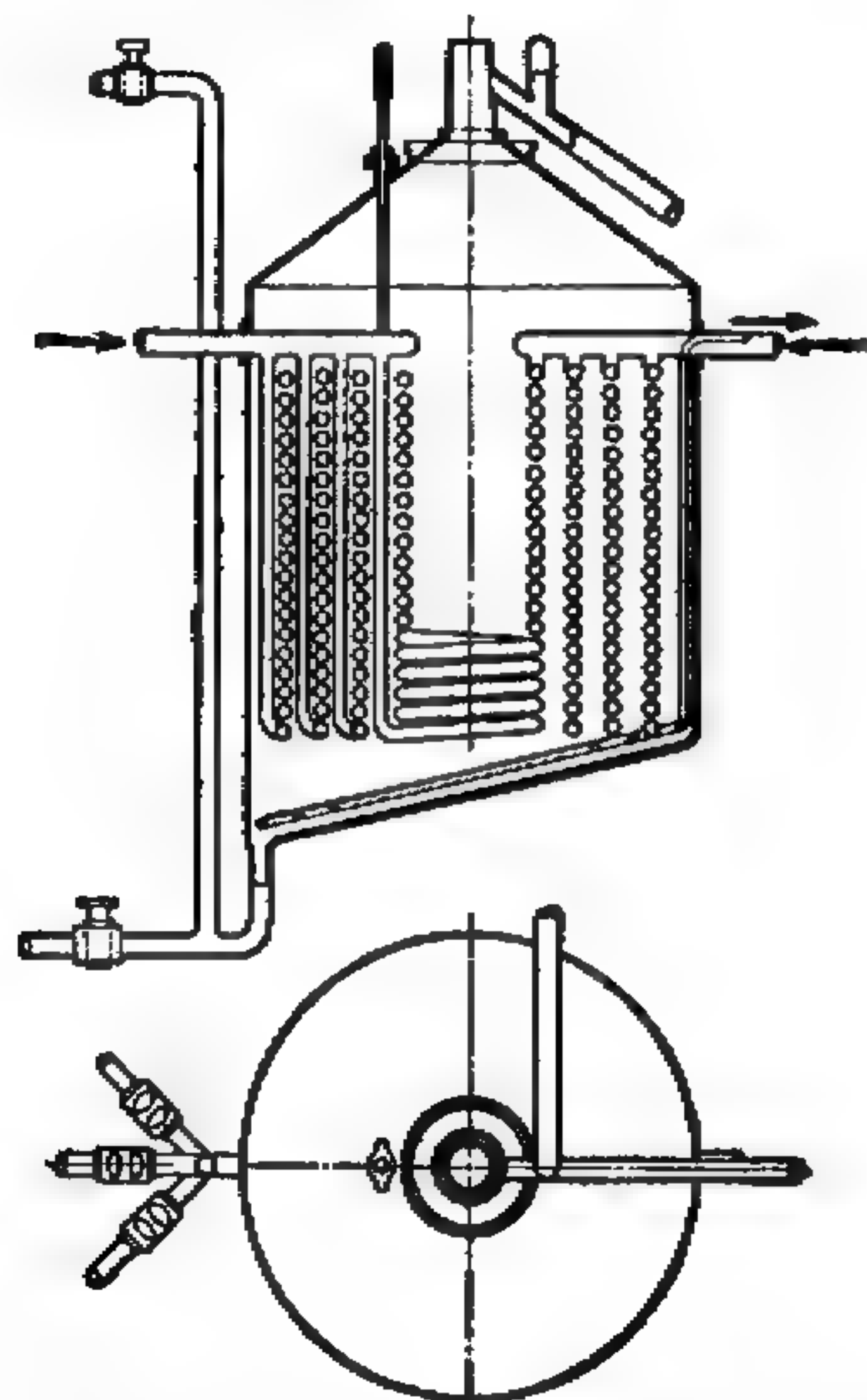


FIG. 11. NATHAN-THOMSON-RINTOUL COMBINED NITRATOR-SEPARATOR

leads downward for the first 30 cm., so that during agitation no nitroglycerine can reach the upright portion. Cooling coils, air agitation and a thermometer are provided as usual. The conical cover with dome, window and overflow to the pre-wash tank correspond to the device just described in the displacement-separator process. The vapor pipe (m) is connected to the lead pipe k as the overflow for the displaced nitroglycerine. The nitration is carried

out as usual, and then after shutting off the air agitation, cooling and waiting a few minutes, the separation is made in the nitrator itself, just as in the displacement process, by gradually allowing the spent acid from the previous operation to run in slowly from below. This absolutely avoids the necessity of passing acid nitroglycerine through a stoneware stopcock. After all the nitroglycerine has passed over, and the sharp line of separation appears, a small amount of spent acid is drawn off to avoid spattering during the agitation, and a little water added gradually while still stirring, 2 per cent of the weight of the spent acid being sufficient, as experience has shown. This raises the temperature 3° for each per cent of water added. It is then mixed for a while by air until the temperature again falls and the level again raised by adding spent acid from the elevated tank until the nitroglycerine overflows. After again waiting a short time until any nitroglycerine which might be clinging to the walls of the vessel, or between the cooling coils, has collected above, this is also displaced. The spent acid is then absolutely free from nitroglycerine, and is drawn off into the pressure tank. From this pressure tank as much of it is forced into the elevated tank as is required in the next operation for displacing the nitroglycerine.

The after-separator, described further on, is absolutely avoided by this process, and in Waltham-Abbey there are now no after-separator buildings.⁴ This addition of water can naturally also be used in other separating processes.

The combined nitrator-separator process avoids the special separator and the difference in elevation between the nitrator and separator otherwise necessary. No other advantage is evident. In particular it cannot be seen why, as has been frequently stated, better yields should be obtained than with other processes using individual separators. On the contrary, with elimination of the after-separator, and a normal period of operation, a portion of the yield must be sacrificed, which yield would be obtained on allowing the spent acids to stand for several days in the after-separator building. As a rule this amounts to several per cent of the glycerine, but is dependent upon the quality of the latter, and as a rule more than pays the operating costs of the after-separator house.

⁴ After-separators have not been used in the United States for many years.—TRANSLATOR.

CHAPTER VI

PURIFICATION OF NITROGLYCERINE

The nitroglycerine coming off the separator is still considerably contaminated by concentrated acids, for the most part dissolved in the nitroglycerine. The amount of this contamination is approximately 10 per cent, so that the crude, acid nitroglycerine, when completely washed and neutralized, loses 10 per cent in weight. The composition of the acids dissolved in the nitroglycerine does not correspond to that of the spent acid. When using fuming sulphuric acid the spent acid will contain about 74 per cent H_2SO_4 , 9 to 10 per cent HNO_3 , and 16 to 17 per cent H_2O , or a sulphuric-nitric acid relation of 9:1, but the nitroglycerine contains mainly nitric acid, so that on neutralizing the acid wash-water with ammonia and evaporating the salt solution a salt mixture is obtained containing about 80 per cent ammonium nitrate and only 20 per cent ammonium sulphate. Therefore the acid wash-water contains sulphuric and nitric acids in the proportion of 1:4.

While the main quantity of acid can be easily washed out of the oil by water alone, the last traces of acid are very firmly retained and can be removed only by a very intensive purification. The larger part of the acid is removed in the so-called pre-wash tank, in which the acid oil meets cold water at about 15°C . with vigorous agitation. The wash water should not be ice cold, since there would then be the possibility of freezing the oil. Due to the high specific gravity, 1.6, it settles rapidly to the bottom, and is then drawn off to the wash tank, which is usually in a separate building.

In order to give nitroglycerine the greatest stability possible and render it suitable for year-long storage even under unfavorable climatic conditions, it is necessary to remove completely all impurities, particularly any traces of acids. In former times mechanical agitation was used for washing, among other things stirrers such as are used in butter churns.¹ Later compressed air was used, which today is in exclusive use and permits of very simple apparatus. This

usually consists of a cylindrical lead vessel or a wooden tank lined with lead, intended for both operations. Frequently cylindrical wooden tanks of pitch pine are used, since they are not attacked by the dilute acids.² Their size is such that the charge of oil fills them about one-third full, while the quantity of water used for washing is exactly the same as the volume of nitroglycerine. The bottom is sloped and at the lowest point there is a stoneware stopcock to draw off the washed nitroglycerine. At some distance above the layer of oil there are one or more stopcocks to draw off quickly the main quantity of the wash-water. Since the volume of the oil layer diminishes during the washing, unless the main quantity of its acid content has been removed by a pre-washing, there are usually two such stopcocks arranged at corresponding heights. They are connected by a rubber hose to a wooden settling box or stoneware settling jugs, in which most of the floating globules of nitroglycerine settle out on the bottom and can be drawn off through stopcocks and returned to the wash tank. The latter has a conical cover, like the nitrator. The cover has glass windows to afford observation of the interior, and inlets for cold, hot water, and soda solution, as well as a fume pipe. A thermometer indicates the temperature. A lead pipe leads to the bottom of the tank for the compressed air, ending either in a perforated spiral, or blowing the compressed air against the center of a lead cone, as described under the nitrator. In order to be able to separate the wash-waters, particularly the soda solution, from the oil layer as completely as possible after the main quantity has been removed through the stopcock, a funnel skimmer is often provided (fig. 12). This consists of a funnel having a welded, cross-shaped handle and ring. A rubber hose is attached to the pointed bottom of the funnel, which leads to a pipe near the bottom of the tank, this latter pipe passing through the walls of the tank and having a stopcock on the outside. A rope is fastened to the handle of the funnel, passing over a pulley on the roof of the building, and fastened by a clamp. If it is desired to draw off the soda solution completely the funnel is lowered into the liquid until it is near the surface of the nitroglycerine, and the supernatant liquid runs out through the hose. Guttman in 1894 attributed an explosion to the sudden dropping of such a funnel weighing 35 pounds on to nitroglycerine heated to 50°C .,

¹ Guttman, *Die Industrie der Explosivstoffe*, pp. 422-423.

² If pitch-pine is not available, oak has been used at times.

the latter being naturally more sensitive at this temperature. For this reason he recommends making the funnel of thin sheet lead, and always holding it up by a counterweight. With charges of uniform size, and stopcocks suitably located, the funnel is not absolutely necessary.

Regarding such wash tanks mention should be made of a process described in British patent 23871 (1910), in which the otherwise necessary difference in levels of the pre-wash and after-wash tanks is avoided by placing both side by side and connecting them together at the bottom by a pipe. The nitroglycerine can be forced from one

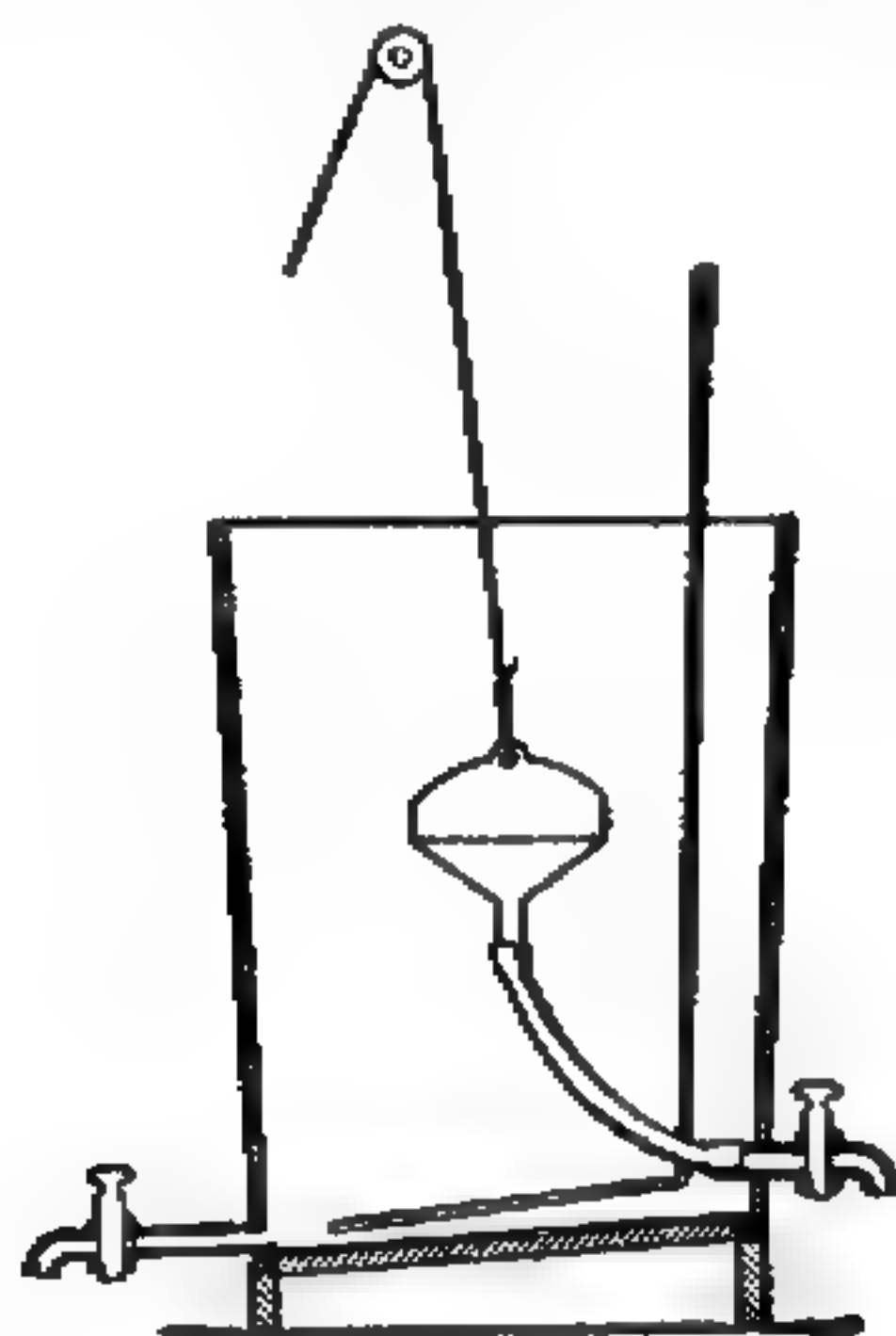


FIG. 12. SKIMMER FOR REMOVING SUPERNATANT WASH WATER

to the other by suitable water pressure. This is useful for plants built on level ground, where there is no natural fall, and even with large charges this permits moderate heights of the buildings.

While the first, or so-called drowning wash, is always made with cold water,³ several washes with water at gradually increasing temperatures follow. It can be readily understood that the more fluid nitroglycerine at the higher temperatures permits washing out the last traces of acids, particularly nitrous acid, more readily than would cold nitroglycerine. Cold and hot water are mixed together so that the desired temperature is obtained. In the course of three to four

³ In the United States this wash is at 38 to 43°C.—TRANSLATOR.

changes of water the temperature of the charge is raised to 30 to 40°C., at each temperature agitating vigorously for about five minutes, then allowing to settle a few minutes, and drawing off the wash-water.⁴ Since it is extraordinarily difficult to remove the last traces of acid even with many changes of water, it is quite customary to then agitate vigorously for a somewhat longer time (fifteen to twenty minutes) with a hot, dilute sodium carbonate solution, the water of the solution being added hot enough to bring the entire charge to a temperature of about 50°C.⁵ With sufficient pre-washing a soda solution of 2 to 3 per cent strength is satisfactory. A higher concentration does no good, and wastes sodium carbonate. It can even be a disadvantage, because in such a case the nitroglycerine is slowly attacked and partly saponified. It has also happened that with too much soda and formation of an emulsion from the attack upon the nitroglycerine the settling is retarded. On the other hand, the idea expressed by Guttman, for example, that the use of hot soda solutions is not advisable, is not substantiated. As stated, the low strength solution hardly attacks the nitroglycerine, the volatility of the latter at 50°C. does not affect the yield, and injury to the operator from evaporation of the warm nitroglycerine can be almost completely avoided by a proper sealing of the cover and a suitable ejector in the fume pipe. Adding soda at the very beginning of the washing, as was formerly done at many places, is of no advantage because of the violent foaming it causes as long as large amounts of acid are present, and gives an unnecessarily high consumption of soda. A red coloration on adding a few drops of an alcoholic solution of phenolphthalein shows an excess of soda. This excess must be carefully removed, because any soda remaining in the nitroglycerine has an unfavorable effect upon the stability, and on the other hand while the nitroglycerine is freshly-made it can indicate a stability higher than the actual. For this reason one or more subsequent washes are given with luke warm water after the soda solution has been drawn off as completely as possible. The finished oil should then have a completely neutral reaction to moist litmus paper. If this is not the case the water washes, or even the soda washes, must be repeated. The ease with which nitroglycerine can be stabilized to satisfy the various requirements of the heat test is dependent upon the quality of the glycerine

⁴ Only one water wash is given in the United States.—TRANSLATOR.

⁵ Here the maximum temperature permitted is about 43°C.—TRANSLATOR.

used. A sample of the finished product then usually goes to the laboratory, where it is subjected to the so-called Abel test which is described in more detail under "Chemical Properties."⁶ Nitroglycerine intended for the manufacture of explosives for domestic consumption is usually considered satisfactory if it is neutral to litmus. On the other hand, if it is intended for the manufacture of smokeless powder it must pass rigid specifications for stability toward heat. In this case it must not discolor extremely sensitive zinc iodide-starch paper within twenty minutes at 50°C. Nitroglycerine intended for use in explosives to be subjected to severe heat must withstand ten minutes at 72°C. with potassium iodide-starch paper without bluing (see Abel test). The industry of the world is largely based upon this requirement.

FILTRATION OF NITROGLYCERINE

The waste nitroglycerine is filtered to remove the "heavy impurities and foreign substances." For this purpose rectangular filter boxes with wooden frame and pockets, the covers of which are traversed by long stretched canvas cloth over perforated openings are used. In operation, the filter is covered with a layer of canvas cloth which is a part of the ordinary equipment and is protected from the outside by plugging up of the pores. Moreover, the salt is dissolved away and the waste spent that is present is removed in the process, which is making the oil clear. After being used, the filter is washed away by water, the oil which has been retained is scraped out again, and fresh salt is added to the filter. Also the filter must be washed out with warm water from time to time. It is finally burned and replaced by a new one.

The filter boxes stand directly in front of the wash tanks, the outlet stopcocks of the latter extending over the filter frame. The filter boxes also have an outlet stopcock at the bottom, usually covered rubber through which the oil is drawn out into a gutter from which it runs via a lead pipe to the point where it is to be used, for example, the

⁶ The Abel test was dropped by the larger companies about 1910 in the United States. No test is now made except for absolute neutrality, which is required for foreign countries. Translation.

⁷ No filtration of nitroglycerine has ever been done in the United States. Translator.

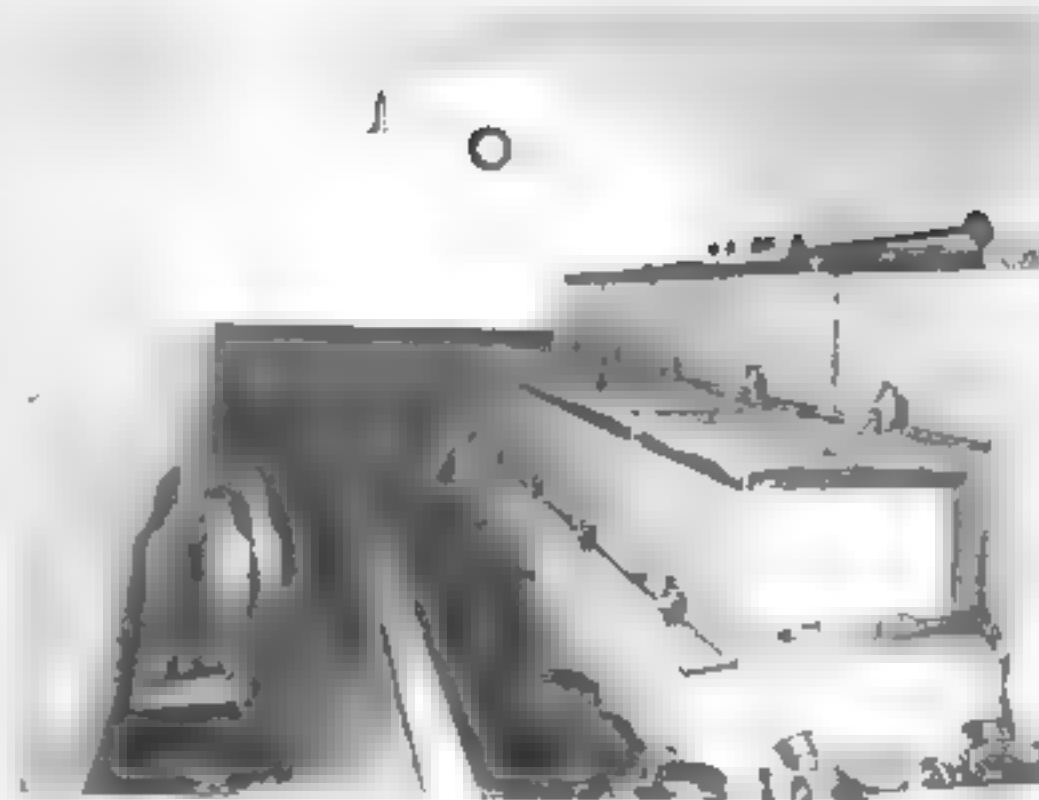


FIG. 3. NITROGLYCERINE FILTER BOX



FIG. 4. FILTER HOUSE.

mixing house. Since such pipes can propagate an explosion from one building to another arrangements are made to break the connection for a space—at least one meter. This break being connected together when necessary to use the pipe by a piece of rubber hose. Even then, however, there is danger of propagation of explosion while the nitroglycerine is running down the pipe.⁸ For this reason the oil is frequently drawn off into hard rubber tanks placed in a depression of the base beneath the filter boxes and carried to the point of consumption.

In order to avoid too large an accumulation of nitroglycerine in the wash house the filtering is performed in a special filter house, which then serves as an oil storage and is entered only for the purpose of removing nitroglycerine. It is weighed there into buckets in the desired amounts. In the filter house there are two rows of boxes, one above the other. The nitroglycerine from the wash house runs through the pipes into the upper filter box or is poured into it via a short pipe after being run in from outside the barrack. From the upper filter box the oil runs away over the filter into the lower box, from which it is drawn out for use.⁹

The suspended water which at first makes the nitroglycerine milky in appearance and which is only partly removed by the filter separates almost completely after standing several days and the oil becomes perfectly clear. It is placed in gas-tight storage in well-ventilated rooms. After some days the oil still contains not more than 0.3 to 0.4 percent of water, at this condition it can be safely used for all explosives. Even the traces filtered on as a residue thus have more than 0.7 percent of water,¹⁰ of which the greater part can be evaporated by the heating of the thin layers in the wash agitators during the preparation of gelatin explosives. In other respects a small amount of water in nitroglycerine, contrary to certain prejudices, does not affect the gelatinization of nitrocellulose.

⁸ To avoid the possibility of propagation the nitroglycerine is drawn off into tanks on rubber-tired wagons and pushed along a ways away from the point of consumption. It is taken the place of carrying over in buckets since charges of dynamite or gelatine as big as 700 kg. are exploded at one time and carrying by buckets would be expensive. (Translator.)

¹⁰ A fine wash water saturated common salt solution according to the same result as gelatinization as regards final moisture content. (Translator.)

CHAPTER VII

CLARIFICATION OF THE WASTE WASH-WATERS

The wash-waters drawn off the nitroglycerine carry with them no inconsiderable quantity of suspended nitroglycerine, which must be carefully removed before they are discharged into drains or streams. Years ago, when the danger lurking in them was not sufficiently appreciated, or the clarification process incomplete, there was a peculiar accident in the vicinity of a dynamite plant located directly on a river, when a boatman struck his pole, shod with iron, violently against a rocky bank, and together with his boat, was blown into the air by a violent explosion. The wash-waters from a nitroglycerine plant emptied at just this point, and apparently because of insufficient clarification a large quantity of nitroglycerine had gradually settled in a rocky depression in the bank, and did not sink into the stony ground nor dissolve because of the great insolubility of nitroglycerine in water. Usually there are small overflow boxes with a dividing wall between them, located right in front or at the side of the wash tanks, with stopcocks at the bottom, through which the waste waters run, while the greater part of the suspended oil sinks to the bottom. It is then removed from time to time and returned to the wash tank. Lead overflow boxes are not recommended here because they are too readily attacked by the initially strong acid water. Long, rectangular stoneware boxes are customarily used. In plants where two large wash tanks in one building receive the product of two nitrators there is a large wooden tank with several intermediate walls located between and below the wash tanks. The water runs from both left and right into this latter tank and finally overflows from it. At the lowest point of the inclined bottom of the tank there are stopcocks to remove the nitroglycerine which has settled out. Final clarification of all the wash-waters is done in a special building, the so-called waste-water house, which contains tanks of such a size or number that a slow passage of large quantities of water through them completely removes the last traces of small drops of nitroglycerine. The acid and alkaline wash-waters

unite here. However, the alkalinity of the latter is insufficient to neutralize all of the wash-water, so that acid wash-water goes to waste. Wooden or stoneware jugs are used here. Often large wooden tanks several meters in diameter, subdivided by many cross partitions, are used. The partitions have alternate upper and lower perforations to make the flow reverse its direction frequently and allow the nitroglycerine to fall to the bottom. The latter is drawn off from time to time through one or more suitably located stopcocks. Such overflow tanks are preferably long and wide, so that on passing the water through them all of the nitroglycerine will collect at one point, the lowest, and can be drawn off very easily. The recovered nitroglycerine, since it is derived from the various stages of the washing process, is not pure, and is put back into the wash tanks, with the fresh oil so that it will be stabilized. It is best to add only small quantities of such recovered oil to a single charge in the wash tank, because the recovered oil contains all kinds of impurities such as fatty acids and mucilaginous bodies, which as experience has shown, float on the wash-water, and when too much of these are added to a charge an emulsion forms on washing, with consequent poor settling. In recent times a series of ten or twelve rectangular stoneware jugs with overflow partitions and outlet cocks at the bottom have been used frequently in the clarification plant instead of the large wooden tank. They are arranged in cascade in the form of a horse shoe, along both sides of the building. The partitions have alternately upper and lower openings, so that the water is forced to follow a long path, just as with the wooden tanks (see fig. 14).

UTILIZATION OF THE ACID WASH-WATERS

The fact mentioned at the beginning of this section, namely that considerable quantities of acids, particularly nitric acid, can be lost with the wash-waters, and in large plants can contaminate the ground water or streams, has in recent times led to proposals to recover these acids in the form of salts, and so completely avoid acid wash-waters. One of these proposals is German patent 325944 (1918) by Hofwimmer.

It consists in treating the acid nitroglycerine directly with a saturated alkali nitrate solution containing sufficient alkali carbonate to neutralize the free acid present. The foaming caused by the evolution of free CO_2 is avoided

by using a quantity of carbonate sufficient to form the bicarbonate. Naturally the wash-waters are used over and over, and the excess of alkali finally extracted by washing with water. Complete elimination of waste waters, as claimed by the inventor by the use of the after-wash-waters in the preparation of new carbonate solutions, is impossible because larger quantities of water are necessary for the final purification of the nitroglycerine and the attainment of a satisfactory stability. It should be noted that nitroglycerine is more readily soluble in the first, strongly acid wash-water than in pure water, and that by the "salting out" action of the concentrated solution, which has been saturated with nitroglycerine by repeated use, there is a reduction in the loss and an increase in the yield. On the other hand, evaporation of the portion of the wash-waters removed for recovery of the salt mixture is of only a limited value. No other utilization of it is mentioned. In any case it can serve for the manufacture of nitric acid, since it contains mainly the nitrate. When using it as a fertilizer the excess of alkali may be injurious, while the sulphate is merely inert.

Such a use is claimed by German patent 339031 of October 8, 1918, issued to the Dynamit A.-G. vorm. Nobel & Co., for a process of purifying crude nitroglycerine, in which the extracted acids are neutralized by ammonia and the ammonia salt solution obtained used for washing fresh charges of nitroglycerine and consequently attaining a concentration after several operations which makes its evaporation and recovery of the salts profitable. Finally, a portion of the solution corresponding to that of the ammonia solution required is removed, with a concentration of 50 per cent, giving about 8 kg. of a mixture of about 70 per cent ammonium nitrate and 30 per cent ammonium sulphate per 100 kg. of nitroglycerine. This mixture is a fertilizer rich in nitrogen. It is better if the neutralized nitroglycerine is extracted in the usual manner with hot soda solutions, and then water, for thorough stabilization, in order to completely remove the impurities frequently found in the salt solutions used. Thus only a slightly alkaline wash-water is obtained, while the acids are recovered without loss and acid wash-waters are avoided. At the same time the nitroglycerine yield is raised about 2.5 per cent because instead of several wash-waters there is a single pre-wash with a salt solution already saturated with nitroglycerine from previous operations.

Another utilization of the waste waters from nitroglycerine plants is the object of German patent 299030, issued to the Westfälisch-Anhaltische Sprengstoff A.-G. It depends upon the fact that these wash-waters contain considerable quantities of dissolved nitroglycerine. The solubility of the latter in water at ordinary temperatures is about 2 grams per liter, so that a cubic meter of wash-water, assuming that all the wash-waters have been previously well saturated with nitroglycerine, will contain about 2 kg. of nitroglycerine, and also some dinitroglycerine. As a matter of fact, 4 to 5 grams of pure oil can be extracted from a liter of these wash-waters by the use of ether, which, aside from unstable impurities, consists mostly of a mixture of nitroglycerine and dinitroglycerine. Naturally any recovery of this small quantity of nitroglycerine by the use of an organic solvent is uneconomical. The pat-

ented process covers extraction of the dissolved nitroglycerine from the wash waters by treatment with nitrocellulose. It is known that collodion nitro-cotton takes up readily liquid nitroglycerine suspended in water, as in the manufacture of ballistite. Tests by the author have shown that the claims of the inventor are not correct, and that even on long standing the collodion nitrocotton does not take up the dissolved nitroglycerine. Even if this were the case the process would hardly cover the operating costs, because all the impurities present in the acid wash waters would be precipitated, requiring a subsequent purification of the collodion nitrocotton.

CHAPTER VIII

AFTER-SEPARATION

In the esterification of glycerine to glycerine trinitrate by adding the glycerine to a mixture of nitric and sulphuric acids the velocity of reaction is at first extraordinarily high. It diminishes with decreasing concentration of the HNO_3 molecules and finally becomes so small that the end point of the reaction when the last molecules of nitroglycerine form is only attained very gradually. The result of this is that the separation of the last traces of nitroglycerine from the spent acid takes place gradually and only after the main quantity has separated. In addition to this, if nitrated at temperatures of 25° to 30°C ., a subsequent cooling of the spent acid, with consequent lowering of the nitroglycerine solubility coefficient, causes a further separation of a small quantity. This gradual, subsequent separation of small quantities of oil after the separation of the main quantity is called "after-separation." It can amount to 2 per cent of the total yield and 5 per cent of the glycerine used. Its amount and period is not dependent upon the velocity of the reaction alone, but is dependent also upon the quality of the glycerine and the nature of the impurities therein. Otherwise it would be always the same with the same quantity of acid of a uniform composition. The quality of, and the impurities in the glycerine govern the extent of the difficulty of separation of the last traces of nitroglycerine from its emulsion with acids. Some glycerines give much, some little nitroglycerine after-separation. However, the amounts are always worth while, both from an economic and a safety point of view, since an acid which is still separating out nitroglycerine should not be taken from the barricaded area of the nitroglycerine plant nor further worked up, as in denitration. The after-separation takes place in a special building, and aside from the necessity of so doing because of the above-mentioned danger, its operation is economical even on a small scale because it does not cost much. The operation consists merely

in maintaining the equipment, and wages for one operator, who looks after the work and watches the process constantly.¹

Large lead, conical-topped tanks having the shape and principle of operation of the displacement separator are used for the after-separation. The upper, conical part of the tank ends in a wide glass tube, about 10 cm. in diameter and 30 cm. high, cemented in, which permits of differentiation of the kind of liquid therein. It is open at the top, or occasionally provided with a fume exhaust pipe. At its lower part, or about a third of the way up, the glass tube has a glass stopcock cemented in, or merely a glass tube inserted and cemented into the side and inclining downward sharply. As a rule the level of the liquid reaches the height of this stopcock or side-tube. A lead pipe enters the bottom of the vessel, and the apparatus is filled with spent acid from the separator via the latter. Moreover, this lead pipe connects with a small, elevated supply tank containing spent acid which has already been subjected to after-separation. A stopcock, located at a suitable place, serves to replenish the acid. Some time after the tank has been filled with freshly-separated spent acid an accumulation of nitroglycerine appears at the top of the glass tube. Then the operator with his left hand carefully opens that stopcock through which the liquid rises up into the glass tube, and with his right hand holds a porcelain, lead or aluminum vessel under the overflow pipe and collects the displaced nitroglycerine. As soon as the visible line of separation between oil and acid nearly reaches the height of the lateral overflow tube he closes the stopcock and leaves the liquid at rest until a layer of nitroglycerine has again collected at the top. From time to time this is also drawn off, without allowing large quantities to collect at any one time. The acid oil is immediately brought under water in a stoneware jug and freed from the main quantity of acid by repeated changes of water and compressed air agitation. It is then carried in guttapercha boxes to the wash-house for final stabilization.

The conical head of the after-separator tank preferably has a ring-shaped lead attachment forming a gutter with an outlet around the

¹ In the United States no after-separator is used. With clean, well-settled nitrating acids and the quality of glycerine now obtained, the amounts of nitroglycerine recovered became so small in the after-separator that they were hard to find. Very low temperatures of nitration and separation contribute toward this end.—TRANSLATOR.

cone. This prevents the liquid running on to the floor in case of a too rapid opening of the stopcock, or an overflow of oil and acid over the rim of the glass tube if there is a development of gas inside the apparatus. The tanks have inclined bottoms and a large stoneware stopcock at the lowest point, which can be connected to the drowning tank or to the pipe leading to the pressure tank, from which the after-separated acids pass on to further operations. The use of drowning tanks in connection with after-separation is infrequent today, since with the present acid concentrations, which leave only small quantities of unnitrated glycerine as such in the spent acid, and since the latter with their relatively low water contents have little or no tendency to start oxidation, a decomposition of any considerable extent in the after-separator can hardly occur. At many places the latter contain cooling coils in order to be able to cool if necessary by a water circulation, but the danger from unnoticed leaks in such coils almost overbalances their advantages, so that they are not in general use. Also wooden cooling jackets around the after-separator are not any longer in general use since wood is everywhere avoided as much as possible in buildings, except where absolutely necessary, because it can catch fire from overflowing acid. For this reason even the floor is usually covered with lead. Frequently air agitation is provided in order to be able to overcome any possible local overheating.

There are usually on each side of the long building a series of such tanks, often able to receive the output of two operations and containing as much as 2000 to 3000 kg. It is a rule to make the size of the installation large enough to receive the whole output of several days. Although by far the greater part of the oil will be drawn off on the first day, nevertheless the spent acid separates small quantities of oil for several days, so that if possible it should be allowed to stand for eight or ten days. It should be a universal regulation that an operator watches the plant day and night, constantly removing the acid nitroglycerine, since on long standing it can always decompose and the accumulation of large quantities can lead to an explosion.

In the English government powder plant at Waltham-Abbey the after-separation has been completely eliminated, as stated above, by adding a few per cent of water to the separated spent acid and so greatly displacing the equilibrium between nitroglycerine on the

one hand and nitric acid-sulphuric acid-water mixtures on the other hand, that no further formation and separation of nitroglycerine can occur.

EXTRACTION OF THE WASTE ACID

Another method of avoiding after-separation and still obtaining a satisfactory degree of separation of nitroglycerine which would otherwise be recovered by after-separation is covered by German patent 250444 (1910).

According to this patent the spent acid after separation is treated with chloroform, which takes up the finely emulsified and dissolved nitroglycerine. Only a small quantity of chloroform is required for this extraction. By the addition of a small quantity of paraffin oil, which mixes with the chloroform but in which the nitroglycerine is insoluble, an almost complete separation of the latter from the chloroform occurs when it is washed with water to remove the acids extracted at the same time. The preliminary removal of the acids is necessary because they attack commercial grades of paraffin oil and the resulting products contaminate the nitroglycerine.

On a large scale the use of this seemingly simple process gives economic difficulties. The operating costs of extraction, washing of the solution, and recovery of the chloroform by distillation from the paraffin solution may be considerably higher than the cost of recovery of the nitroglycerine by simple standing of the spent acid in the after-separator tanks, quite aside from the fact that the loss of the expensive, volatile solvent cannot be wholly avoided in the various steps. The elimination of the relatively small operating danger of after-separation is balanced by the danger of a subsequent after-separation of unstable nitroglycerine at higher temperatures during the distillation of chloroform from the paraffin oil, because the separation is by no means complete and the mixture of paraffin oil and chloroform still contains some dissolved nitroglycerine almost insoluble in paraffin oil. Even after preliminary after-separation the spent acid still contains some dissolved nitroglycerine, which can be recovered by the chloroform treatment, accompanied by a small amount of dinitroglycerine, which increases the total yield based upon glycerine by about three or four per cent. However, this increase may not cover the operating costs, and nothing is known regarding the practical use of the patented process.

CHAPTER IX

DENITRATION OF THE SPENT ACIDS

After complete separation of the nitroglycerine, the spent acids consist of a concentrated mixture of sulphuric and nitric acids, usually of the following composition:

73 to 74 per cent H_2SO_4 , 9 to 10 per cent HNO_3 , 16 to 17 per cent H_2O

If ordinary sulphuric acid is used instead of oleum in making the mixed acid the water content of the spent acid becomes 20 per cent. In addition it contains some nitroglycerine and lower glycerine nitrates dissolved in it, as well as a small amount of nitrous acid.

On account of the danger of a subsequent separation of further small quantities of nitroglycerine, particularly on strong cooling, such spent acid is not transported, but every nitroglycerine plant has a denitrating equipment where this acid is separated into its components, namely sulphuric and nitric acids. On denitration the sulphuric acid is usually obtained as a 56°Bé or 72 per cent acid, and the nitric acid as 38 to 40°Bé or 57 to 62 per cent HNO_3 . It is either concentrated further in special devices, or used in the manufacture of ammonium nitrate or aromatic nitrocompounds as cases may require, while the sulphuric acid is concentrated by the well known process and used for charging acid in the nitric acid retorts or as absorption acid in oleum plants, or sold without further concentration as spent sulphuric acid to fertilizer plants.

Denitration, or the driving off the nitric acid and nitrous acid from the sulphuric acid, is done in a so-called denitrating tower. Formerly cast iron retorts, set in suitable furnaces and heated by direct fires, or even direct heated horizontal cast iron denitrating towers into which steam and compressed air were passed, were used. These devices were long ago replaced by the continuous denitrating tower consisting of iron lined with a strong acid-proof brick, or even a cylinder of acid-proof material such as volvic stone. This tower is filled with Guttman balls, pieces of quartz, stoneware, Raschig rings or other material to subdivide the descending liquid, and at the

upper part has a distributing plate into which the spent acid runs, via a baffle box and a safety funnel to separate any residues of nitroglycerine which may be present. These must be carefully watched, because any nitroglycerine entering the denitrating tower can cause an explosion. Superheated steam is passed into the bottom of the tower,¹ meeting the descending current of finely divided spent acid, and the sulphuric acid flows downward, freed from all but traces of

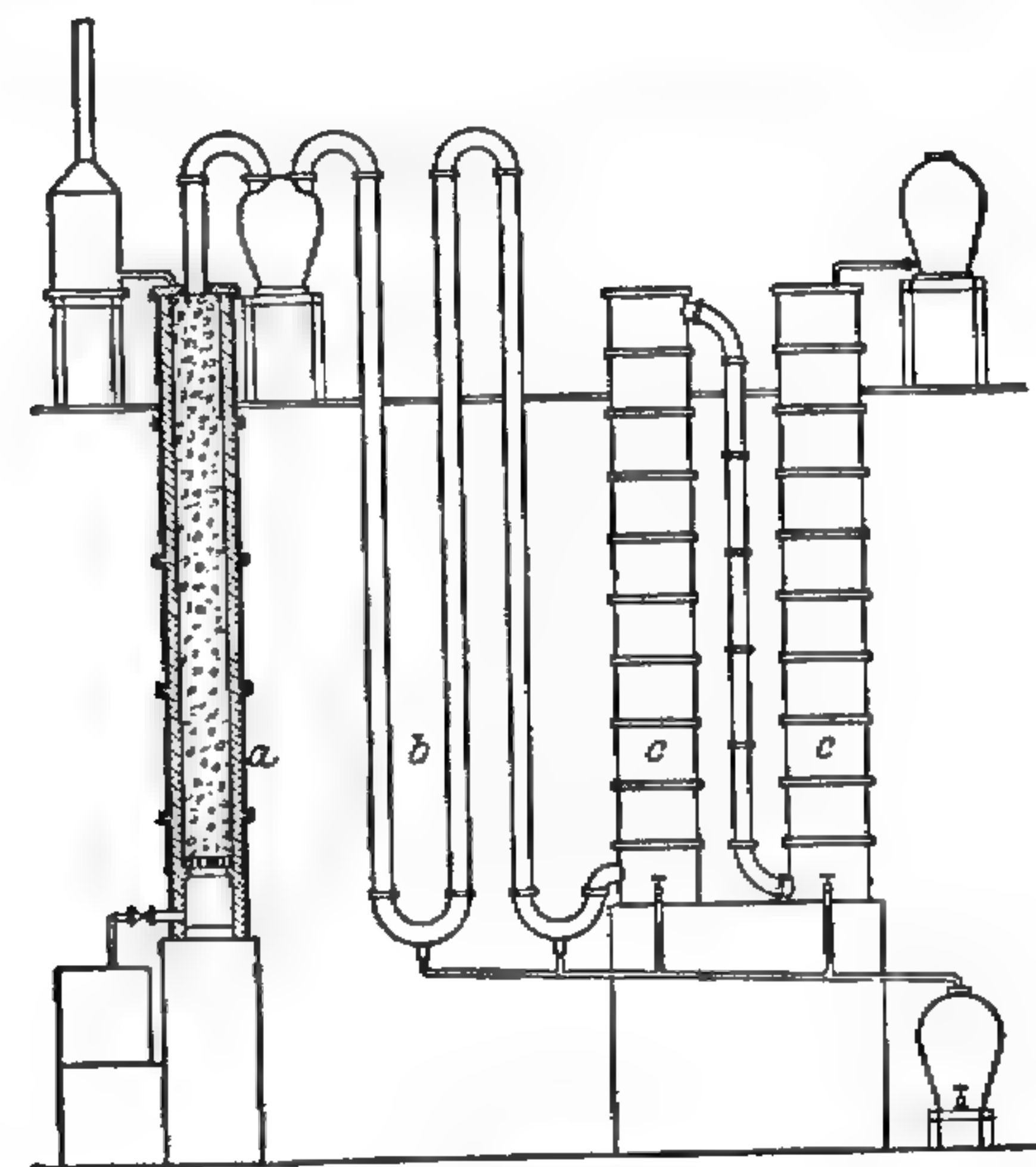


FIG. 15. DENITRATION

(a) Denitrating tower, (b) air condenser, (c) absorption towers

nitric and nitrous acids, the latter being formed in considerable quantities by an oxidation of the organic compounds in the spent acid, while the nitric and nitrous acids escape at the top of the tower as a gas, today condensed by a tube condenser but formerly in tourilles. By blowing in air by an injector the nitrous acid is oxidized

¹ In the United States no superheat is used, the cost of the latter in general not overbalancing the smaller quantity of water added to the sulphuric acid when superheated steam is used.—TRANSLATOR.

to nitric acid, and the remaining gases are finally condensed to a weak nitric acid in a Lunge absorption tower by spraying them with water. The operation can be so conducted that 38 to 40°Bé nitric acid is obtained in both condenser and towers.² The injected steam should have as high a temperature as possible, in any case above 300°C. The higher the temperature the less the steam required for complete denitration and the less the dilution of the acids. A denitrating tower of the usual size will denitrate about 5000 kg. of spent acid per twenty-four hours.³

A special form of denitrating tower is described in German patent 182216 issued to Evers, in which reaction towers are used, not completely filled with packing, but divided into several chambers by perforated divisions alternately packed and empty. In the empty spaces moving mixers as described in German patent 145743 are arranged for the purpose of giving a particularly thorough mixing of the drops of liquid with the hot gases. On account of their delicate nature these mixing devices are frequently omitted in actual practice without apparently affecting the final result. A highly heated mixture of air and steam is blown by injectors into the various chambers. In order to heat the air it is passed through the hot denitrated sulphuric acid as it leaves the foot of the tower, and the air is then heated to 400°C. in a special furnace. The steam is likewise superheated in a coil. The repeated diffusion and thorough mixing of the acids and gases in the empty spaces gives a very uniform denitration. It is said to produce a water-white sulphuric acid of 60°Bé, four-fifths of the nitric acid as 40° acid and one-fifth as 36° acid, with only 0.3 per cent nitrous acid and very small losses. An Evers denitrating plant is said to denitrate 20,000 to 22,000 kg. of spent acid per twenty-four hours with a coal or coke consumption per 100 kg. of acid of not more than 45 kg.⁴

According to French patent 405819 (1909) issued to Vender, it is

² By returning the weak nitric acid to the top of the denitrating tower and feeding it in with the spent acid, a nitric acid containing 90 to 95 per cent HNO_3 can be condensed, the balance of the water passing down with the denitrated sulphuric acid.—TRANSLATOR.

³ A brick-lined tower 24 feet high and 23 inches internal diameter will denitrate 120,000 to 140,000 pounds of spent acid per twenty-four hours.—TRANSLATOR.

⁴ *Z. Schiess- u. Sprengstoffw.*, 1907, p. 144.

of advantage to use for denitration the gases coming from electric furnaces used for the oxidation of atmospheric nitrogen.

A special method of treatment of spent acid is described in German patent 180587 (1906), issued to the Salpetersäure-Industriegesellschaft at Gelsenkirchen, in which the spent acid is electrolyzed as the anode liquid, while dilute nitric acid is used as the cathode liquid. The nitric oxides formed at the cathode are conducted to the anode and with the oxygen set free there and the dilute nitric acid form strong nitric acid, so that the spent acid can finally be regenerated to its original concentration. German patent 180052 (1905) is another form of this process, in which dilute nitric acid is concentrated by electrolysis by liquefaction in a condenser of the nitric oxides formed at the cathode, and adding them to the nitric acid surrounding the anode, so that they are oxidized to the monohydrate. The use of spent acid is said to have the advantage of requiring a lower current consumption than pure nitric acid, because of the better conductivity of the spent acid containing sulphuric acid.

OTHER METHODS OF USING NITROGLYCERINE SPENT ACIDS

There has been no lack of proposals for the direct use of nitroglycerine spent acids instead of decomposing them by the so-called denitration, by using the nitric acid content in true nitration reactions. While the esterification of the alcohols by mixtures of nitric and sulphuric acids is a reversible process which requires a considerable excess of nitric acid for completion, the conversion of aromatic hydrocarbons like benzene or toluene to nitrobenzene or nitrotoluene by substitution is irreversible, in which nitroglycerine spent acids containing about 10 per cent HNO_3 can be used almost quantitatively by mixing such acids with the corresponding quantity of benzene or toluene.

For example, to nitrate on part of toluene to the mono-stage requires theoretically about 7 parts of spent acid containing 10 per cent HNO_3 . As a matter of fact, by mixing the corresponding quantity of spent acid and toluene and cooling, then heating to about 40°C., about 90 per cent of the theoretical yield of nitrotoluene can be obtained. It is natural to use the nitroglycerine spent acids as above and so save the cost of denitration in such plants as may manufacture the nitroderivatives of toluene or benzene in addition to making nitroglycerine. Dinitrotoluene and trinitrotoluene play an important part in the manufacture of explosives, and for this reason they are made by the

various explosive plants in their own installation. The fear that nitroglycerine spent acid, even after proper after-separation, may still separate small quantities of nitroglycerine and thus be a source of danger in another operation can be very simply avoided by adding 2 to 3 per cent of water to it and displacing the equilibrium between the dissolved residues of nitroglycerine and glycerine sulphate, so that the nitroglycerine is decomposed and a further separation of the latter rendered impossible. On the other hand, the high excess of sulphuric acid and water content of the spent acid affects the yield somewhat, because the nitrotoluene yield can amount to 97 to 98 per cent when using nitrating acids of the proper composition. This may be the reason why plants which produce both nitroglycerine and nitrotoluene have up to the present time preferred denitration of the spent acid to the above-described method.

CHAPTER X

OPERATING RESULTS

According to the theoretical decomposition equation, 92 parts of glycerine and 189 parts of nitric acid monohydrate form 227 parts of nitroglycerine and 54 parts of water, so that 100 parts of glycerine and 205.43 parts of nitric acid must form 246.74 parts of nitroglycerine and 58.7 parts of water, or for 100 parts of nitroglycerine 40.53 parts of glycerine and 83.26 parts of HNO_3 are theoretically required, forming 23.79 parts of water.

However, the theoretical result is never obtained in practice. If only the theoretically required quantity of nitric acid were used the results would be very unsatisfactory, even with a sufficient quantity of the dehydrating agent, sulphuric acid, since by no means all of the nitric acid molecules present would form nitroglycerine. This process is rather a reversible one, and nitroglycerine dissolves in concentrated sulphuric acid, splitting off nitric acid molecules and forming glycerine sulphate or lower glycerine nitrates until the nitric acid molecules have reached a concentration such that if they be increased nitroglycerine will again be formed and the solution as well as the decomposition of the same come to a standstill or state of equilibrium.

From this it is evident that from the very first a definite excess of nitric acid must be present in order to convert all of the added glycerine to nitroglycerine. This excess must be so chosen that after addition and solution of the total quantity of glycerine in the acid mixture a spent acid will be formed still so rich in nitric acid molecules as to exert no destructive action upon the nitroglycerine. This relation has been determined by experience. In commercial practice there must be considered, in addition to the chemical factor of the tendency of the resulting spent acid to form or decompose nitroglycerine, the purely physical factor of the solubility coefficient of the spent acid of nitroglycerine. Spent acids of different compositions have very different solubilities for nitroglycerine, and an overwhelming excess of nitric acid is not the most advantageous for the highest

possible nitroglycerine yield, although theoretically the glycerine should be the more completely converted into nitroglycerine the greater the quantity of nitric acid present. Since nitroglycerine is readily soluble in pure, concentrated nitric acid, its solubility in a mixed acid increases somewhat above a certain limit with increasing HNO_3 content.

Therefore the following conditions govern practical attainment of the highest possible nitroglycerine yield, namely quantity and composition of the nitrating acid so chosen that after conversion of the glycerine a minimum of that spent acid must be obtained which has the lowest solubility for nitroglycerine.

TABLE 2
Solubility and decomposing powers of various compositions

	ACID MIXTURE					
	I	II	III	IV	V	VI
	per cent	per cent	per cent	per cent	per cent	per cent
H_2O	20.0	15.0	10.0	5.0	10.0	15.0
HNO_3	10.0	10.0	10.0	15.0	15.0	15.0
H_2SO_4	70.0	75.0	80.0	80.0	75.0	70.0
Dissolved nitroglycerine.....	6.00	3.55	3.33	4.37	2.60	2.36
Nitroglycerine extracted by chloroform.....	2.47	1.46	1.92	2.13	1.65	1.72
Difference, or nitroglycerine decomposed.....	3.53	2.09	1.41	2.24	0.95	0.64

* Per 100 parts of acid mixture.

SOLUBILITY OF NITROGLYCERINE IN WASTE ACIDS OF DIFFERENT COMPOSITIONS

The most favorable composition of the spent acid has been determined in the course of time by experience and countless studies on the most advantageous nitrating conditions. To reduce the quantity of spent acid produced to the lowest possible degree and thus suffer the least solubility loss of nitroglycerine is merely a question of the concentration of the acids available. It immediately becomes evident that in general the operating results have improved as the industry came to the point where it was able to produce economically the most highly concentrated acid. The greatest advance in better utilization of glycerine was, as already mentioned above, when a number of large plants at the close of the last century began to use fuming

sulphuric acid containing 20 to 25 per cent free SO_3 in place of ordinary English sulphuric acid containing 94 to 96 per cent H_2SO_4 . With one stroke the yields were improved by about 15 per cent of the glycerine, i.e., from about 210 to 225 per cent, because the higher concentration permitted an appreciable reduction in the total quantity of acid used without an increased use of nitric, so that a smaller quantity of spent acid was obtained, having also a more favorable composition as regards nitroglycerine solubility.

A review of the solubility and decomposing powers of various compositions of spent acid on nitroglycerine is given in table 2, based upon tests made by the author with synthetic acid mixtures. Therefore the best mixture is VI, with 15 per cent H_2O and 15 per cent HNO_3 , and the worst I, containing relatively large amounts of water and little nitric acid. The latter represents approximately that spent acid obtained before the introduction of oleum. Acid II represents approximately the composition when using oleum.

For example, with one of the older nitrating acids composed of 300 parts of 90 per cent nitric acid and 450 parts of 94 per cent sulphuric acid, or a total of 750 parts of mixed acid containing 36 per cent HNO_3 , 56.4 per cent H_2SO_4 , and 7.6 per cent H_2O per 100 parts of glycerine, the theoretical conversion of the latter into 246.7 parts of nitroglycerine will give the following spent acid:

	parts	per cent
HNO_3	270.0	
HNO_3	-205.4	
HNO_3	64.6	10.7
H_2SO_4	423.0	70.1
H_2O	115.7	19.2
Spent acid.....	603.3	100.0

The composition of this acid approaches that of mix I.

Therefore 600 parts must dissolve 36 parts of nitroglycerine and break it up. Instead of 246.7 parts of nitroglycerine only about 211 can be separated. If consideration is taken of the few per cent lost in the wash-water, and the fact that dynamite glycerine is not 100 per cent pure, and that during nitration without artificial cooling and with acids containing water there is a certain amount of oxidation, it can be seen that the yields are only 205 per cent of the glycerine instead of the theoretical 246.7 per cent, in spite of the excess of nitric acid in the above case. On the other hand, if oleum and one of the new nitrating mixtures is used, for example 280 parts of 92 per cent nitric acid and 350 parts of oleum containing 20 per cent free SO_3 (or 104.5 per cent H_2SO_4), or 630 parts of a mixed acid containing 41 per cent HNO_3 , 58 per cent H_2SO_4

and 1 per cent H_2O per 100 parts of glycerine, the following theoretical spent acid will be obtained:

	parts	per cent
HNO_3	257.6	
HNO_3	-205.4	
HNO_3	52.2	10.8
H_2SO_4	365.7	75.7
H_2O	65.4	13.5
Spent acid.....	483.3	100.0

which is approximately the composition of the above synthetic acid II, having a solubility of about 3 per cent. Therefore 483 parts must dissolve and break down 14.5 parts of nitroglycerine, so that 232 parts of the latter separate. As a matter of fact, such a mixed acid gives a practical nitroglycerine yield of 226 to 227 per cent of the glycerine.

UTILIZATION OF GLYCERINE

The technical result of the better utilization of the glycerine at even higher concentrations of the mixed acids is evident from the following nitration made by the author on an experimental scale:

A quantity of 285 parts of 95 per cent nitric acid and 215 parts of 50 per cent free SO_3 oleum, or a total of 500 parts of a mixed acid containing 54.14 per cent HNO_3 , 8.84 per cent SO_3 and 37.02 per cent H_2SO_4 gives the following theoretical spent acid with 100 parts of glycerine:

	parts	per cent
HNO_3	65.3	18.5
H_2O	48.8	13.8
H_2SO_4	239.2	67.7
Spent acid.....	353.3	100.0

If the same solubility coefficient as in the above synthetic acid VI is assumed, the loss from dissolved and decomposed nitroglycerine is 8.5 parts, so that $246.7 - 8.5 = 238.2$ parts of nitroglycerine, which must separate. As a matter of fact the author, with this mixed acid and chemically pure glycerine nitrating at 0 to $10^\circ C$. with good cooling, obtained a practical nitroglycerine yield of 234 per cent of the glycerine, or about 95 per cent of theory. If consideration is taken of the loss of 4.3 parts of dinitroglycerine contained in the nitroglycerine and lost in washing, as can be determined by extraction of the wash-waters, actually 238.3 parts of nitroglycerine have separated, corresponding to the theory when deducting the solubility loss in spent acid. From this spent acid 3.8 parts of nitroglycerine containing dinitroglycerine were extracted. Taking into consideration the small quantity of dinitroglycerine determined by the nitrogen determination and contained in the oil extracted from the wash-water and spent acid, this nitration is a conversion of 98.4

per cent of the glycerine to nitroglycerine and dinitroglycerine. The small remainder may be partially oxidized and partially remain in the spent acid as glycerine sulphate.

The degree of utilization of the glycerine finds a practical limitation from the economy point of view, which under certain conditions can prevent raising the excess of nitric acid up to the limit of the highest attainable yields if only an insignificant improvement results, because the increased use of nitric acid does not pay. In general, however, the relation between the costs of glycerine and nitric acid has been such in recent times that it pays to so choose the excess of nitric acid as to give approximately the highest yield, because such an excess of nitric acid will be largely recovered as concentrated nitric acid in denitration, while the unused glycerine is irrevocably lost. The most economical composition in the last analysis is found for each plant by tests with various compositions and consideration of ruling prices of glycerine and acids and the value of the recovered acids. The case of concentration of the acids is quite different. Here the cost of manufacture of a nitric acid exceeding a concentration of 93 to 94 per cent monohydrate and an oleum containing more than 25 per cent free SO_3 (produced by distillation of the fuming sulphuric acid first obtained) is always so high that nitrating acids like III, in spite of their higher nitroglycerine yields, can hardly be used in actual practice.^{1,2}

After all, the use of 93 to 94 per cent nitric acid and 25 per cent oleum, and so absolutely water-free or even anhydrous mixed acid containing 40 to 42 per cent HNO_3 , is no longer any rarity today in the manufacture of nitroglycerine.

ARTIFICIAL COOLING

In addition to the highest possible acid concentration of the mixed acid there is another important factor in the operating results, namely the efficiency of cooling and the nitrating temperature. With a given temperature of the cooling water a larger cooling surface permits a reduction in the nitrating time or the nitrating temperature.

¹ The use of oleum containing 40 per cent free SO_3 is practically universal in the United States.—TRANSLATOR.

² Today in Germany also 500 parts of an acid mixture of 50 per cent HNO_3 and 50 per cent H_2SO_4 per 100 parts of glycerine are generally used with a yield of 233 to 235 per cent of nitroglycerine.—AUTHOR.

The reverse holds true for colder cooling water and a given cooling surface. Too long a period of nitration reduces yields on account of the large quantity of nitric acid blown out by the compressed air.³ The lowest possible temperature of nitration limits side reactions and consequently raises the nitroglycerine yields. For this reason attention has been given to providing as large a cooling surface as possible in the nitrator, and the latter has at times been constructed very large in proportion to its charge in order to contain numerous cooling coils. Efforts are also made to have as cold a cooling water as possible. For example, plants located along streams pump the ice-cold river water into special reservoirs to provide the plant with cooling water. In the last decade nitroglycerine plants have even been provided with refrigeration plants and a cooled common salt or calcium chloride brine at -10 to -12°C ., which is circulated through the cooling coils instead of water. This allows nitration to be done in the same period of time at 12 to 15°C . as would be the case at 25 to 30°C . Lower temperatures than this are not used on account of an apprehended danger of forming crystals of nitroglycerine.⁴ The increased yield of about 4 per cent of the glycerine has seemed to be worth while with the high glycerine prices of recent years.

If it is mainly a question of the greatest possible output of a plant, by using artificially cooled brine and the usual nitrating temperature of about 30°C . the glycerine can be fed in more rapidly and a considerable reduction in time of nitration realized, which naturally increases the rate of production.

Since in the shorter nitrating period less nitric acid is blown out by the compressed air, with a given acid there will be an increase in yield, or vice versa, a saving in nitric acid.⁵

The effect of nitrating temperature upon the yield varies con-

³ This is not the case if mechanical stirring is used, as in the United States.—TRANSLATOR.

⁴ In the United States, with calcium chloride brine at -23 to -18°C . in the cooling coils, nitration of both glycerine and mixtures of glycerine and polyglycerine or sugar is done at 2 to 3°C ., with no formation of nitroglycerine crystals, because the freezing point of mixtures of nitroglycerine and acids is lower than the true freezing point of nitroglycerine alone. Such nitrating temperatures improve yields and increase output, overbalancing the cost of artificial refrigeration.—TRANSLATOR.

⁵ This does not apply to mechanical stirring, which is universal in the United States and has been for many years.—TRANSLATOR.

siderably with the water content of the mixed acid. Tests with a mixed acid containing 39 per cent HNO_3 and 5.5 per cent H_2O , made without oleum, from 98 per cent sulphuric acid, gave with a nitrating temperature of 30°C . a yield of 205 per cent, at 0°C . 217 per cent, or an increased yield of 12 per cent of the glycerine. An acid containing 38.7 per cent HNO_3 and 2.7 per cent H_2O , or 650 parts of acid to 100 parts of glycerine, gave:

	per cent yield
At 30°C	216
At 10°C	223
At 0°C	225

or a difference of 7 and 9 per cent respectively. On the other hand the difference with water-free, or acids very low in water (below 2 per cent), was only about 4 to 4.5 per cent between nitrating temperatures of 30 and 0 to 10°C .

Plants which have introduced artificial refrigeration have, as a matter of fact, increased their yields about 4 per cent of the glycerine by maintaining a nitrating temperature of about 12°C . In addition to a reduction in the oxidizing action of the nitric acid at the lower temperatures, the latter come into play in the separation by a reduction in the solubility coefficient, as well as from the fact that less nitric acid is blown out of the cold mixed acids than from warm acids by the agitating air. Today the best operated plants, with the best quality of glycerine and by using oleum, obtain nitroglycerine yields of 226 to 227 per cent with nitrating temperatures of 25 to 30°C ., and 230 to 232 per cent when using artificial cooling and nitrating temperatures of 12 to 15°C . These are 92 and 93.6 per cent of theory respectively.⁶

On the contrary, in the early days of the manufacture of nitroglycerine considerably under 200 per cent of the glycerine was the usual yield. Even in the middle of the seventies of the previous century well operated plants obtained about 200 per cent, and even Guttman mentions in his *Industrie der Explosivstoffe*, appearing in 1895, an average figure of 200 per cent in summer and 205 per cent in winter.

⁶ With the conditions and temperatures used in the United States the average yield during a year has been 234 per cent based upon absolutely dry nitroglycerine.—TRANSLATOR.

CHAPTER XI

PLANT LAY-OUT IN GENERAL

In general, the arrangement of the different buildings of a nitroglycerine plant, their distance from one another and from other buildings, as well as protection by earth barricades, is on the same basis as for powder and explosive plants. The liquid nature of the raw material and products, glycerine, acids, nitroglycerine, spent acid, suggests the use of gravity in handling them. For this reason, where convenient, hillsides or a rolling country are chosen for nitroglycerine plants and the buildings are so arranged that at the highest point there is usually the acid storage and scale for weighing acids, and storage and scales for the glycerine, and from here the buildings are arranged in a series at lower and lower levels. The necessary differences in level increase with the number of stages into which the process is divided, with the size of the operation, and with the distances prescribed between the different buildings. It can be considerable, since the difference in level must not be too small. In plants on level ground excavations and mounds must be used. In such cases the construction of a nitroglycerine plant can involve considerable expense for earth-works, on account of the necessary thickness of the walls. While pressure tanks are almost always used for elevating and moving the acids, when the necessary differences in level are absent the nitroglycerine in some cases has been handled by drawing into empty vessels or by air pressure, in order to be able to run it, for example, from an elevated point in the wash house to a point of similar elevation in the gelatine house. However, this is true only of neutral, purified nitroglycerine.

MASSIVE CONSTRUCTION

The various buildings used for making, storing and preparing the nitroglycerine, the after-separators and waste-water houses, are surrounded by heavy earth walls, often 10 meters thick at the base and about 1 meter at the crown. They reach up to the roof of the buildings, or above, and are covered with grass. Frequently trees

are planted on them. In case of explosion they protect the surroundings to a considerable extent from horizontally flying missiles and force the explosion pressure and fragments upward, thus reducing the distance to which the latter will be thrown. The entrance is via tunnels. Wooden linings of the latter have proven of little use, because they do not satisfactorily withstand the pressure. Today solid masonry or concrete is generally used, unless ziz-zag passages go through the walls. Tunnels, curved or zig-zag to better protect anyone fleeing from the explosion, are popular, but they may not always attain their purpose. In no case may even a zig-zag tunnel connect two buildings. In case of explosion the tunnel can, as experience has shown, propagate the shock from one building to another. The buildings in which nitroglycerine is made, stored or prepared have been up until recently as a rule of light construction and with a light roof, with only the floor of masonry. Only in recent times, or since 1910, has the proposal of C. E. Bichel been adopted, namely of constructing the operating buildings of the nitroglycerine plant of gravel-concrete covered with earth, after tests on it had been made in explosive magazines. In addition to low costs the light construction of the buildings has the advantage that in case of any explosion no heavy missiles are present, because of the more complete disintegration of the material, but on the other hand they are less resistant to falling missiles and the air pressure from adjacent explosions. They are easily pushed in by the latter, the doors jammed and the operators so prevented from getting out readily. Flying missiles can cause fires and explosions by the shock as they strike, or by their heat, and it is not any rare thing with this method of construction to have an explosion extend beyond its source, with more or less complete destruction of the entire plant.

NUMBER OF BUILDINGS

The number of different buildings varies and depends upon the expected production and the size of the charges. An extensive subdivision of the operations, so that each process is carried out in a separate building, can have appreciable advantages as regards serviceability of the plant, yet in Germany it is customary to combine the nitrator and separator in one building.¹ Another building

¹ In the United States also.—TRANSLATOR.

contains the washers and perhaps the filters, while a more distant one contains the after-separator and another the waste water clarifier. Frequently the neutral nitroglycerine runs through lead pipes directly to the storage tanks of the mixing or gelatinizing house, unless a special oil storage is provided, with filters in the same house. Transportation of the neutral oil from building to building is discontinuous in that only during use is there a connection by means of a rubber hose, so that the danger of propagation of explosion is limited to this short space of time.

If nitrator and separator are in one building it is usually prescribed that the two operations shall not be carried on at once. As a rule the nitrator is only filled with acid for the next charge when the acid from the preceding charge has been run out of the separator.

PIPING AND GUTTERS

Pipes for acid nitroglycerine between nitrator and separator buildings, as well as between separator and wash houses, are not without their disadvantages. They require careful installation and cleaning.² In winter then can easily freeze, and in summer direct sunlight, especially if they are not installed quite evenly and have low points, will decompose the stagnant, acid nitroglycerine in the depressions. For this reason low passageways are frequently provided between buildings, through which a man can walk, even if he has to bend over in doing so. In these passageways there is an open lead gutter, heated by steam pipes. If it is desired to avoid such passageways the gutter is supported on posts between the buildings. The pipes are placed in boxes, surrounded by a heat insulator and supported on the posts. Open gutters are covered with wooden covers, and acid gutters with lead covers, to prevent foreign bodies falling into them. Great care must be taken in their installation to prevent stagnation of any nitroglycerine or acids. Since ruptures can occur at the joints, from buckling or too great stiffness with changes of temperature, frequent inspection of the pipes is required, and consequently accessibility. To protect them from freezing in winter a warm water pipe is placed beside the acid or oil pipe. After the nitroglycerine has passed through these pipes they are carefully

² In the United States the gutter is preferred for ease of cleaning.—
TRANSLATOR.

washed out with water, in order to free them as far as possible from this material, and to avoid danger of propagation of explosion.

FLOORS

Special care must be taken with the floors of the work rooms. In the vicinity of the apparatus a lead floor with a rim about one centimeter high is usually placed, so as to be able to clean up easily any acid or nitroglycerine escaping via leaks or as spray, and to prevent the floor from being set on fire from any concentrated acid which may overflow. In order to be able to render any spilled nitroglycerine immediately harmless wooden or hard rubber buckets filled with water and provided with a sponge, are always kept in readiness. The rest of the floor is smoothly planed, closely laid wood, frequently covered with linoleum.

NEW METHODS OF CONSTRUCTION

Recently Bichel³ proposed a complete change in the method of constructing nitroglycerine buildings. He started with the fact that even a decade ago in Germany explosive magazines were constructed not, as formerly, of light wood but of gravel-concrete. These magazines were covered with earth and had the advantage that they were safe against breaking in and theft, offered protection against falling missiles from adjacent explosions, and required no repairs. On an explosion in their interior the gravel-concrete was disintegrated to dust and no large pieces were formed, as was proven by test explosions in such constructions with 1500 and 500 kg. of gelatine dynamite. The proposal consisted in the extension of this method of construction to the manufacture of explosives themselves. Guttman, in his discourse entitled "Twenty Years' Progress in Explosives" had already proposed the same thing, but with this difference, that he proposed reinforced concrete buildings standing in the open but surrounded by walls to afford protection against flying objects and fire. The buildings were to be covered by a horizontal concrete roof, double reinforced by 10 mm. round steel and filled with earth. Quite properly Bichel feared that on explosion of such a building too large pieces would be formed, and that on adjacent explosions they

³ Z. Schiess- u. Sprengstoffw., 1910, p. 182; Bichel., *Neuerungen in der Anlage von Sprengstofffabriken.*

would be crushed in from the heavy roof. Bichel therefore recommended arched construction and burying in the ground completely, and used only a very thin iron net work. At first he limited his proposal to small plants having a moderate output on account of the limited applicability of arches. For a true arch light pumice stone masonry was to be used. The arched buildings which in general are open to daylight only on one side are wholly in the ground or in high barricades and covered with a layer of earth one meter thick. The following advantages are to be expected of this massive construction:

1. In case of explosion within the building few and small missiles. **The unprotected side is protected by a special, high wall.**

2. Great resistance of the different buildings to adjacent explosions.

3. Since the center of explosion, lying deep in the ground, will consume a great part of the energy in destroying the materials of construction and throwing about and disintegrating the surrounding earth, the effect of pressure of the gases of explosion, either far or near, and the corresponding danger will be less.

4. The danger from lightning, which is considerable in explosive plants, must be reduced appreciably by an earth covering.

5. A fire in the building is almost out of the question since only the doors and window frames are of wood, and the rest of the building is incombustible.

6. Flying missiles from adjacent explosions would fall on the earth covering and could not propagate the explosion, as frequently occurs with lightly roofed buildings in the open.

Finally, repair and maintenance costs are practically eliminated by painting the wood and roof. The narrowness of the rooms, their poor lighting, which in cloudy weather often necessitates artificial illumination, their difficult ventilation, and the difficulty of alterations and repairs, are disadvantages.

Although meanwhile the Bichel method of construction has been adopted with good results in some plants it has not been in particularly large plants. They have been content with operations of 100 to 150 kg. of glycerine or 230 to 350 kg. of nitroglycerine per charge, but by building a suitable number of systems in the plant a considerable output has been obtained.

It has been found to be particularly advantageous to conduct the nitration, separation and washing of nitroglycerine in a single arched building, the space relations naturally not permitting of very large



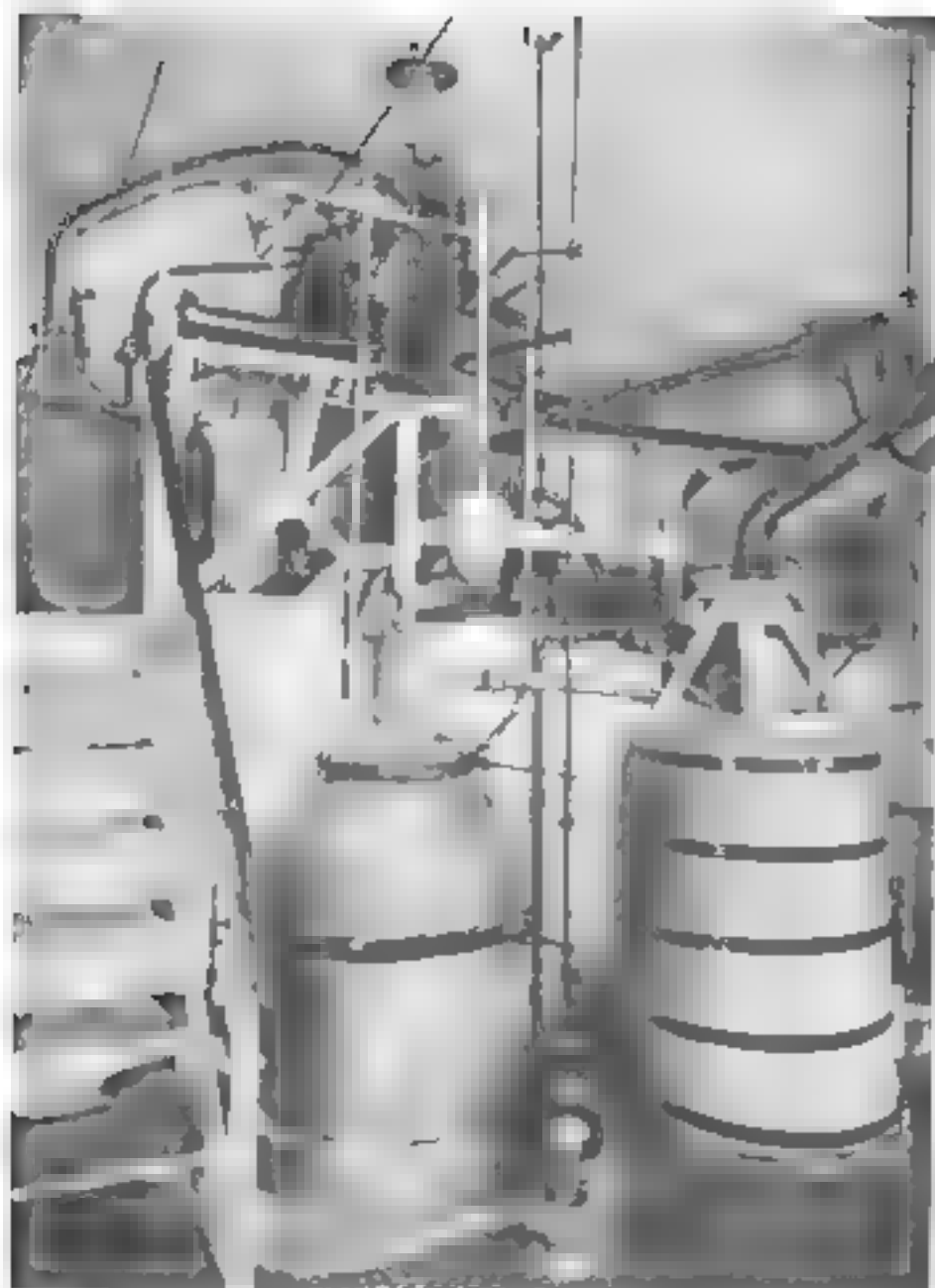


FIG. 7. A CORRUPTED VIEW OF THE FIRST INTERIOR



FIG. 8. A CORRUPTED VIEW OF THE FIRST INTERIOR

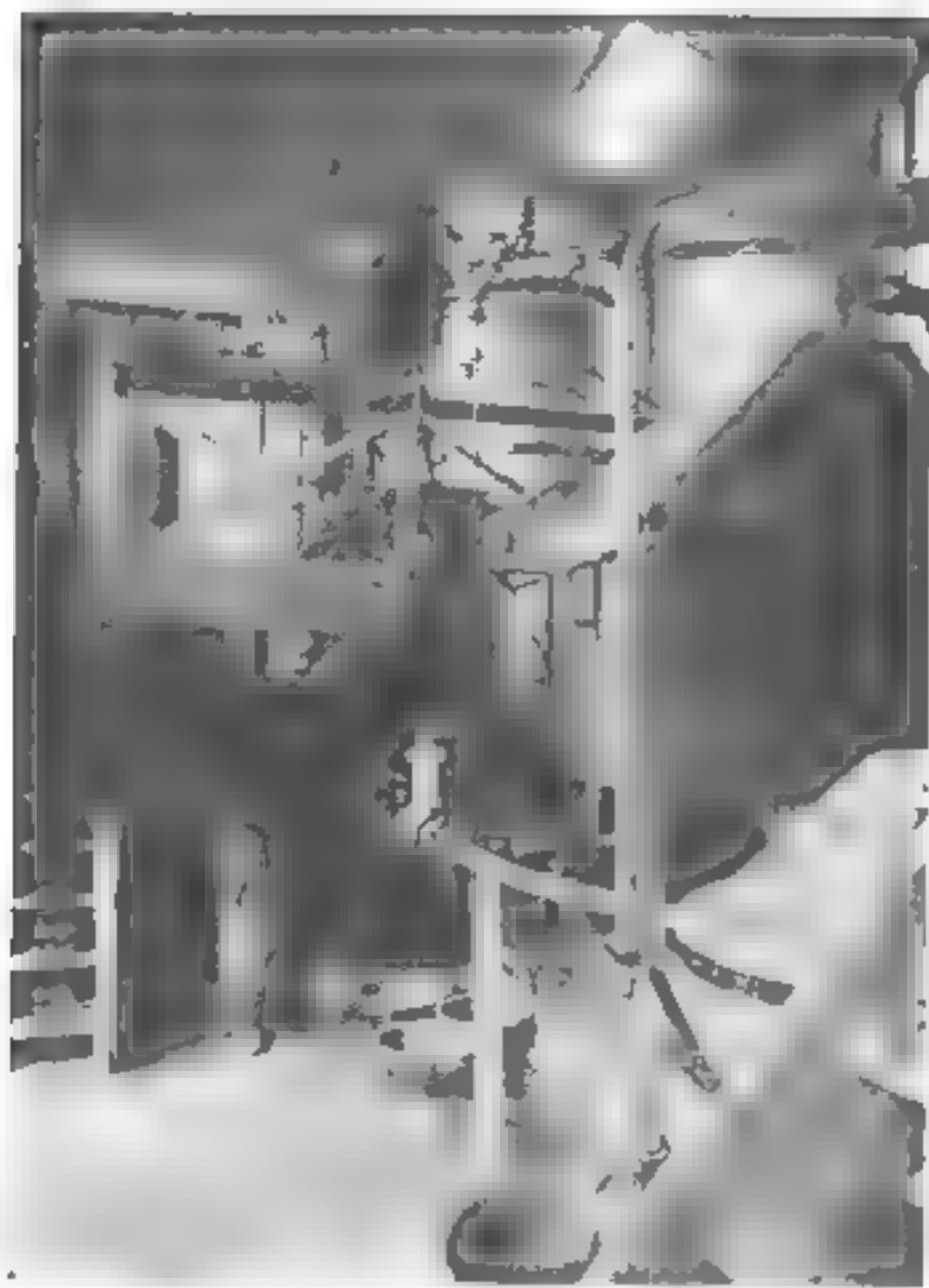


FIGURE 1. CONSTRUCTION OF THE

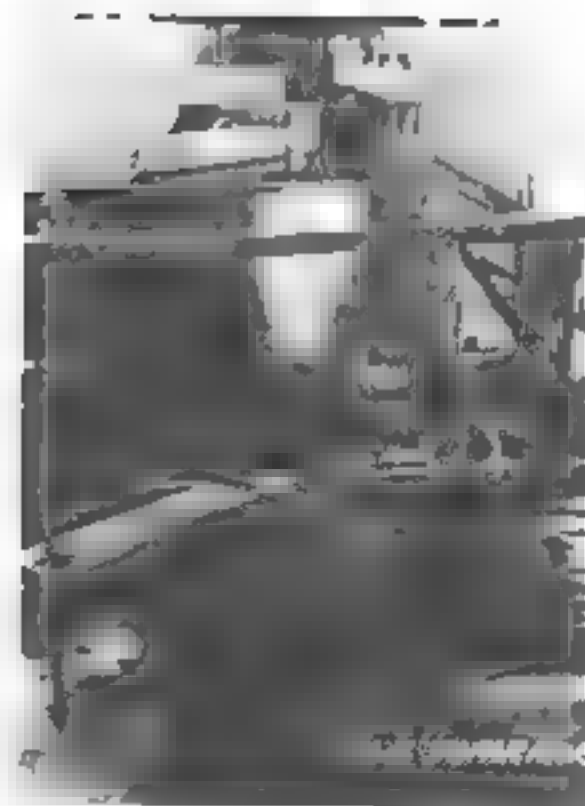


FIGURE 2. CONSTRUCTION OF THE



FIGURE 10. INTERIOR VIEW OF THE BUILDING UNDER CONSTRUCTION.



FIGURE 11. EXTERIOR VIEW OF THE BUILDING.



FIG. 14. BOSTON, MASS.
TAYLOR, MASS.

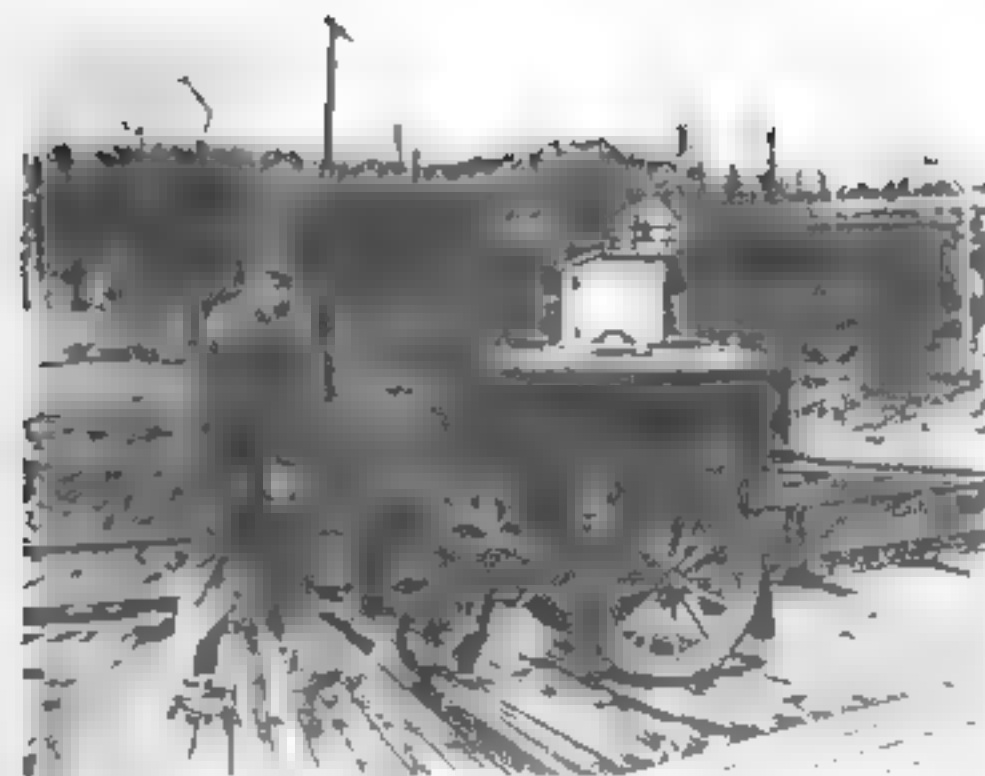


FIG. 15. BOSTON, MASS. (SEE FIG. 14 FOR DETAILS)

charges. For a large output a definite number of such combined systems are laid out, thus giving the advantage that in case any one of the systems is destroyed or suffers an interruption to operations, after repairing the pipes in the other systems production can be continued, whereas with separate loadings for the different operations a destruction of a portion of the plant naturally stops the operation of the entire plant. In this kind of a plant there is absolutely no running of nitro-glycerine from one loading to another, so that a propagation of explosion in this way is excluded. In this kind of plant nitro-glycerine passes from the wash tank through a short pipe through the wall, and in a recess in the wall hard rubber buckets are filled with it and at once taken to a distant storage tank in a safe manner, where the nitration is done. From the weighing department are carried to the granulating or mixing house also by the same principle. Figures 16 to 20 show the method of construction and fitting out of such plants.

This construction principle has proved itself most successful in the last ten years, where the destruction was almost completely limited to the explosion center.



FIG. 16. NITRO-GLYCERINE PLANT.

CHAPTER XII

PHYSICAL, CHEMICAL AND PHYSIOLOGICAL PROPERTIES

PHYSICAL PROPERTIES

Nitroglycerine is an oily liquid, absolutely colorless and water-white in a pure condition. The commercial product is always yellowish or wine-yellow to brownish-yellow, depending upon the depth of the color of the glycerine used, but it is lighter in color than the latter. Absolutely colorless nitroglycerine can be made readily from water-white, chemically pure glycerine and pure reagents and avoidance of high temperatures of nitration and stabilization.

It is odorless at ordinary temperatures, but at temperatures above 50°C. a slight, peculiar odor is perceptible, especially when entering a work room where warm nitroglycerine is being used. Its taste is sweet and burning.

The specific gravity is 1.60 at 15°C., 1.614 at 4°C., and 1.591 at 25°C.¹ Precise determinations by Beckerhinn, 1.5991, and Kast, 1.5995 at 15°/15° come extraordinarily close to the accepted value of 1.60. On freezing it contracts 10/121 of its volume and then has a specific gravity of 1.735 at 10°C. The index of refraction is $n_D = 1.4744$ according to Marpmann.²

The viscosity is 2.5 times that of water and many times less than that of glycerine. The time taken to run out of a 10 cc., pipette at 20°C. is:

	sec.
Water.....	6
Nitroglycerine.....	15
Glycerine.....	540

Volatility. The vapor pressure is extremely small at ordinary temperatures. Only from about 50°C. and up does the volatility become appreciable, so that consideration has to be taken of this factor in analytical work like removal of solvents. Toward 100°C. nitroglycerine is very volatile.

¹ Perkin, *J. Chem. Soc.*, London, vol. 55, p. 685.

² *Apotheker-Ztg.*, vol. 7, p. 312 (1892).

Twenty grams of nitroglycerine in an open weighing glass 70 mm. in diameter lost:

Stored at 50°C. for 24 hours...	0.04 grams, or 0.2 per cent
Stored at 75°C. for 24 hours...	0.32 grams, or 1.6 per cent
Stored at 100°C. for 24 hours...	2 grams, or 10 per cent (abt.)

Thus the volatility at 75°C. is eight times, and at 100°C. fifty times as high as at 50°C. Marshall and Peace³ give the vapor pressure as:

20°	30°	40°	50°	60°	70°	80°	93.3°C
0.00025	0.00083	0.0024	0.0072	0.0188	0.043	0.098	0.29 mm

Ground cordite was used for the determination instead of liquid nitroglycerine, and a definite quantity of air was passed through it at the given temperature. From the loss of weight of the cordite and the quantity of nitroglycerine condensed from the air passed through the stated values were determined. Water vapor raises the volatility.⁴ However, nitroglycerine is relatively difficult to volatilize with steam. Only about 8 grams pass over with one liter of water in a steam distillation.

Nitroglycerine cannot be distilled without decomposition. On heating in a paraffin bath it begins to boil above 140°C. This apparent boiling is due to a rapid decomposition and development of nitrous vapors, giving a distillate of nitroglycerine and dilute nitric acid. Distillation does not take place without decomposition, even in a vacuum, and as far as is known no exact determination of its boiling point has been made.

Melting point. Nitroglycerine crystallizes in two modifications of considerably different melting points, and shows to a high degree the phenomenon of supercooling. This circumstance, and the very low velocity of crystallization may be why the phenomenon of crystallization and the exact crystallizing point of nitroglycerine was determined at a rather late date. S. Nauckhoff⁵ and H. Kast⁶ are to be thanked for exact determinations of this point. Kast found that nitroglycerine may crystallize in two allotropic modifications, or in a labile and stabile form, of which only the first can be converted into the other, which occurs readily, so that there is a monotropic allotropy.

³ *J. S. C. I.* (1916), vol. 109, p. 298.

⁴ Weinberg, *Z. Schiess- u. Sprengstoffw.* (1911), p. 431.

⁵ *Z. angew. Chem.* (1905), p. 11; *Z. Schiess- u. Sprengstoffw.* (1911), p. 124.

⁶ *Z. Schiess- u. Sprengstoffw.*, (1906), p. 225.

Nauckhoff observed only the stabile modification, and in 1905 determined its freezing point as 12 to 12.4°C. for chemically pure, and 10.4 to 10.5°C. for several different samples of commercial nitroglycerine. Later, in 1911, he recognized the higher value given by Kast in 1906 as correct, so that the preparation he formerly considered as chemically pure could not have been pure enough, and the value published by Kast must be considered as correct. Kast gives in table 3 the crystallizing and melting points of both modifications of chemically pure nitroglycerine and for two commercial grades obtained from two different samples of guhr dynamite.

Determination of freezing and melting points. On account of the phenomenon of supercooling, the freezing point cannot be determined

TABLE 3
Crystallizing and melting points of nitroglycerine

KIND OF NITROGLYCERINE	APPEARANCE	NITRO- GEN CONTENT <i>per cent</i>	CRYSTALLIZING POINT		MELTING POINT	
			Labile I	Stabile II	Labile I	Stabile II
Chemically pure	Almost water- white	18.50	2.1	13.2	2.8	13.5
Commercial, from guhr dynamite I.	Yellowish	18.48	2.2	13.1	2.8	13.5
Commercial, from guhr dynamite II.	Yellowish	18.46	1.9	12.3	2.5	13.1

by merely measuring the temperature at which crystallization commences, but it can be determined by observing the highest temperature assumed by a thermometer inserted into a supercooled nitroglycerine when the latter freezes, the crystallization being initiated by seeding with a crystal of nitroglycerine. Nauckhoff operated as follows:

The nitroglycerine in a tube provided with a thermometer and a stirrer, is supercooled by immersing in ice water. After starting the crystallization by introducing a seeding crystal the tube is placed in a larger tube, so that the air jacket protects it from a too rapid loss of heat. Then the apparatus is placed in a water bath whose temperature is somewhat lower than the freezing point of nitroglycerine. During freezing it is stirred, so that only finely divided, solid nitroglycerine forms. At first the temperature rises rapidly, then

slowly, until finally it remains constant at the true freezing point of the nitroglycerine.

The determination of the melting point is somewhat simpler. Nauckhoff used the device shown in figure 21. A glass tube, *a*, with the lower part blown out to a thin-walled pipette with a point 1 mm. long, is partly filled with supercooled nitroglycerine, which is frozen by seeding. The small tube is fastened to a sensitive thermometer, *b*, the point of the tube being opposite the bulb of the thermometer. The whole is then placed in a beaker of water, *c*, the temperature of which is somewhat below the melting point of the nitroglycerine, or about 10 to 11°C. The glass beaker is protected by a larger beaker, *d*, so that the water will not take up heat too rapidly from the surrounding air.

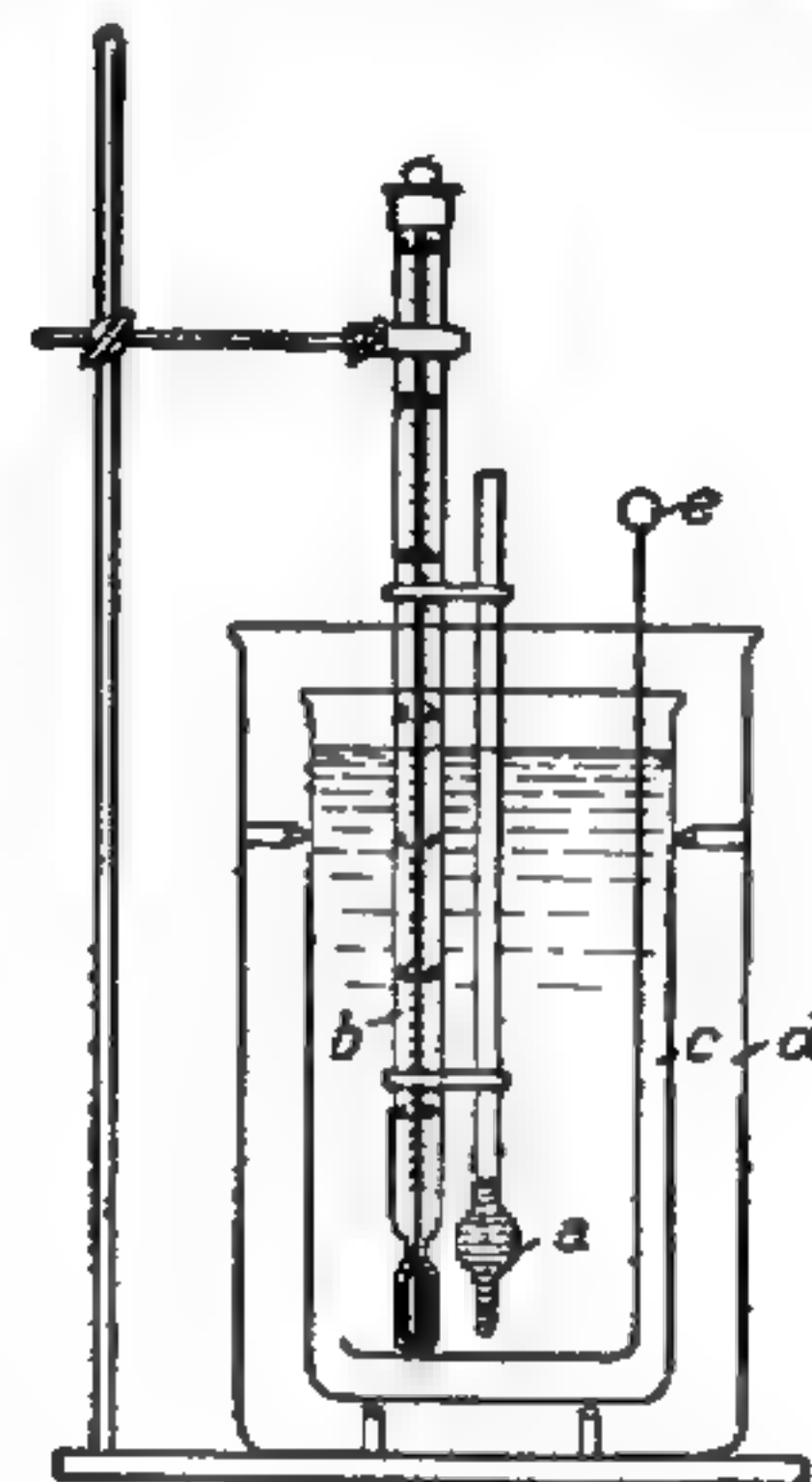


FIG. 21

FIG. 21. NAUCKHOFF MELTING POINT APPARATUS

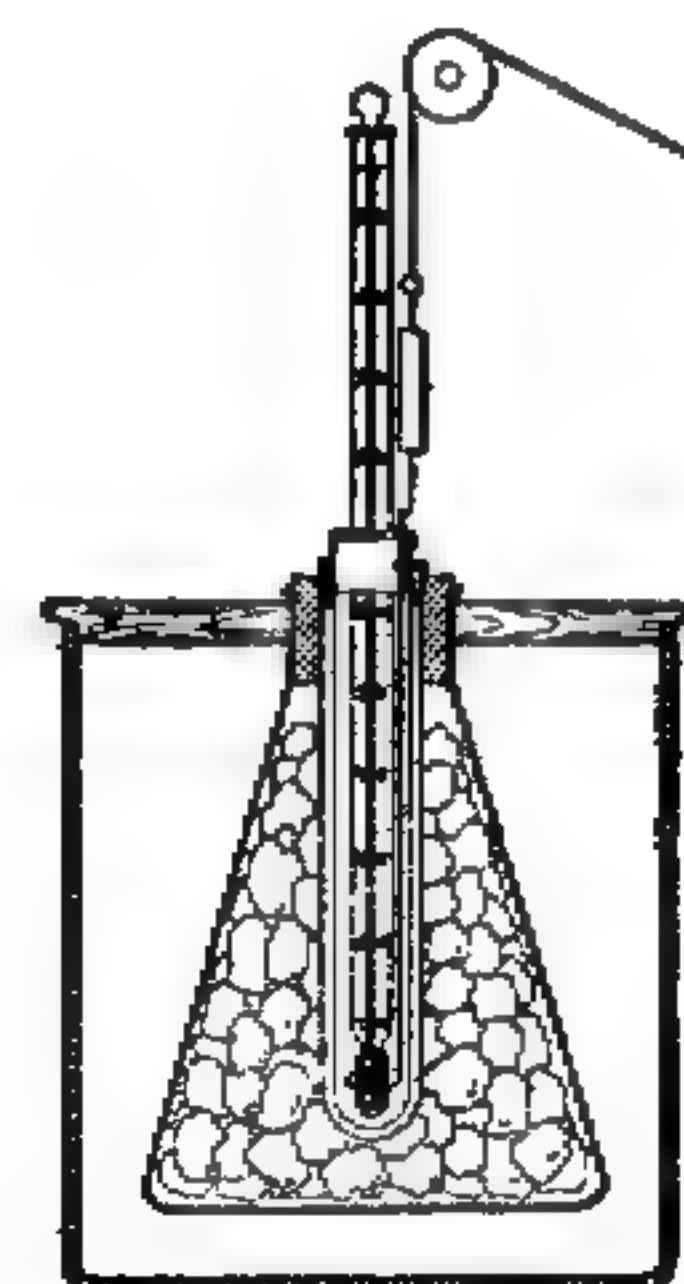


FIG. 22

FIG. 22. KAST MELTING POINT APPARATUS

The temperature of the water rises fast enough when working at ordinary room temperatures. The water is stirred constantly by the stirrer, *c*, and the temperature watched to note that at which the first drop of nitroglycerine shows at the point of the pipette. In order to press out the melted nitroglycerine as it forms, and to keep the frozen nitroglycerine in close contact with the walls of the container the tube is filled with water.

Kast used a similar device, figure 22, to determine freezing, or crystallization, and melting points. In the first case a freezing mixture is employed, and in the second water at a suitable temperature.

To determine the freezing point 15 cc. of nitroglycerine are placed in a wide test tube, *a*, provided with a thermometer, *t*, and a mechanical stirrer, *r*,

surrounded by a second similar test tube, *b*, to insulate it by a layer of air, and firmly held in place by two rubber rings, *g*. Both test tubes are inserted into a wide-mouthed Erlenmeyer flask containing the freezing mixture, *c*, which is in turn suspended in an empty battery jar, *e*, having a wooden cover. After the nitroglycerine has cooled sufficiently, or to about 8° below the crystallizing point, a seeding crystal is added and the thermometer watched while stirring constantly. The highest temperature is taken as the crystallizing point.

The same apparatus is used to determine the melting point, the freezing mixture being merely replaced by water at a suitable temperature. That temperature is taken as the melting point at which the frozen mass begins to become transparent enough to render it possible to see the thermometer from the outside. This point coincides exactly with that point at which the temperature begins to rise rapidly after it has previously remained constant to within a few tenths for a long time.

According to Kast the melting point is more or less above the crystallizing point, depending upon the purity of the nitroglycerine, and can be fairly sharply determined, so that the various values agree to within one- or two-tenths of a degree. On the other hand, the crystallizing point is found to be dependent upon the speed with which the crystallization starts and proceeds.

Hibbert⁷ continued these investigations, and gave the crystallizing points as 1.9° and 13.0°, and the melting points as 2.0° and 13.2° for the labile and stabile modifications respectively. This small difference from Kast's observations is of no practical significance, and can be explained by different methods of reading, assuming equally pure products were used.

As regards the temperature interval between crystallizing point and melting point Kast⁸ mentions at another place that such will be found even with the purest of substances if the point taken as the melting point is the point at which the whole mass is molten.

The interval actually is not present, but is due merely to the manner of carrying out both determinations, since in one case the medium is at a higher, in the other case at a lower temperature than the material to be tested. The height of both points is thus dependent upon the temperature of the surrounding medium. But while the crystallizing point under the given conditions, with pure substances, is always determined sharply to within 0.1°, with the melting point determination there is always a more or less wide field of melting, the wider the more impure the product. In the same sense the interval between crystallization and melting points becomes greater.

⁷ Eighth International Congress of Applied Chemistry, New York, 1912, 4, 37; and *Z. Schiess- u. Sprengstoffw.* (1914), p. 83.

⁸ *Spreng- und Zündstoffe*, p. 165, Vieweg und Sohn, 1921.

Supercooling and velocity of crystallization. According to Tammann⁹ the spontaneous crystallizing powers, expressed by the number of spontaneously forming crystallization centers in a unit of weight of the supercooled liquid per unit of time at a given temperature, and the linear crystallization velocity, i.e., the distance to which the limits between crystallized and liquid states move in a given time unit, govern the supercooling properties of a liquid. The spontaneous crystallizing properties of nitroglycerine are not known, but are apparently very small. Since its linear velocity of crystallization is also very small, the ease of supercooling is very appreciable. To bring small quantities of nitroglycerine into spontaneous crystallization is extremely difficult unless it has been previously crystallized and thawed without large temperature rises. Small quantities of nitroglycerine can be subjected to freezing mixtures for long periods without freezing. The same is true of nitroglycerine explosives. On very strong cooling in a mixture of solid carbon dioxide and ether nitroglycerine is converted into a solid, glassy, amorphous state, but it becomes a thin liquid again on warming to below its crystallizing point. Crystallization occurs more easily with large masses, apparently because the possibility of forming centers of crystallization is increased. Thus it happens that the freezing of dynamite shipments in long transportation at winter temperatures, or stored in unheated buildings in winter, is a quite common phenomenon, and the thawing of the dynamite before use is frequently necessary. Nitroglycerine once frozen always freezes spontaneously and immediately when cooled below its freezing point, i.e., without seeding, provided that it has not been strongly heated in thawing. After thawing it apparently remains in a physical state different from the usual condition, which can be ascribed to definite molecular vibration paths. On the other hand, if thawed nitroglycerine samples are heated for some time to 50°C. this condition disappears, and the usual supercooling phenomenon now appears on cooling below the crystallizing point.

The linear velocity of crystallization was measured by Nauckhoff¹⁰ at various temperatures, and found to be very small:

+5°C.	0°C.	-5°C.	-17°C.
0.145	1.183	0.267	0.125 mm. per minute

⁹ Tammann, *Z. f. physikal. Chem.* (1898), vol. 25, p. 442.

¹⁰ *Z. angew. Chem.* (1905), p. 16.

In general this velocity rises with falling temperatures, but on the other hand it falls with increasing viscosity, and at temperatures below -5°C . the latter effect seems to predominate, according to Nauckhoff's measurements. This agrees with the observations in practice, where pipes carrying nitroglycerine freeze most easily with gentle frosts.

The labile and stabile crystalline forms. Kast, who in his investigations usually crystallized nitroglycerine in the form of guhr dynamite, was unable to determine any regularity in the formation of the labile or stabile forms, but did find that chemically pure nitroglycerine is more difficult to crystallize, but that it always crystallizes in the labile form, and that a less pure nitroglycerine on the other hand freezes more readily but mostly in the stabile form.

On contact with a crystal of the stabile form the labile form goes over into the other form immediately, or without such contact after a certain time. Thus it happens that in actual practice frozen dynamite always contains nitroglycerine in the stabile form, and up until the discovery of Kast only the latter, i.e., that of the higher melting point, was known. The labile form can be differentiated from the stabile form by its glassy appearance, but better by its rapid melting in a water bath heated to 6 to 8°C .

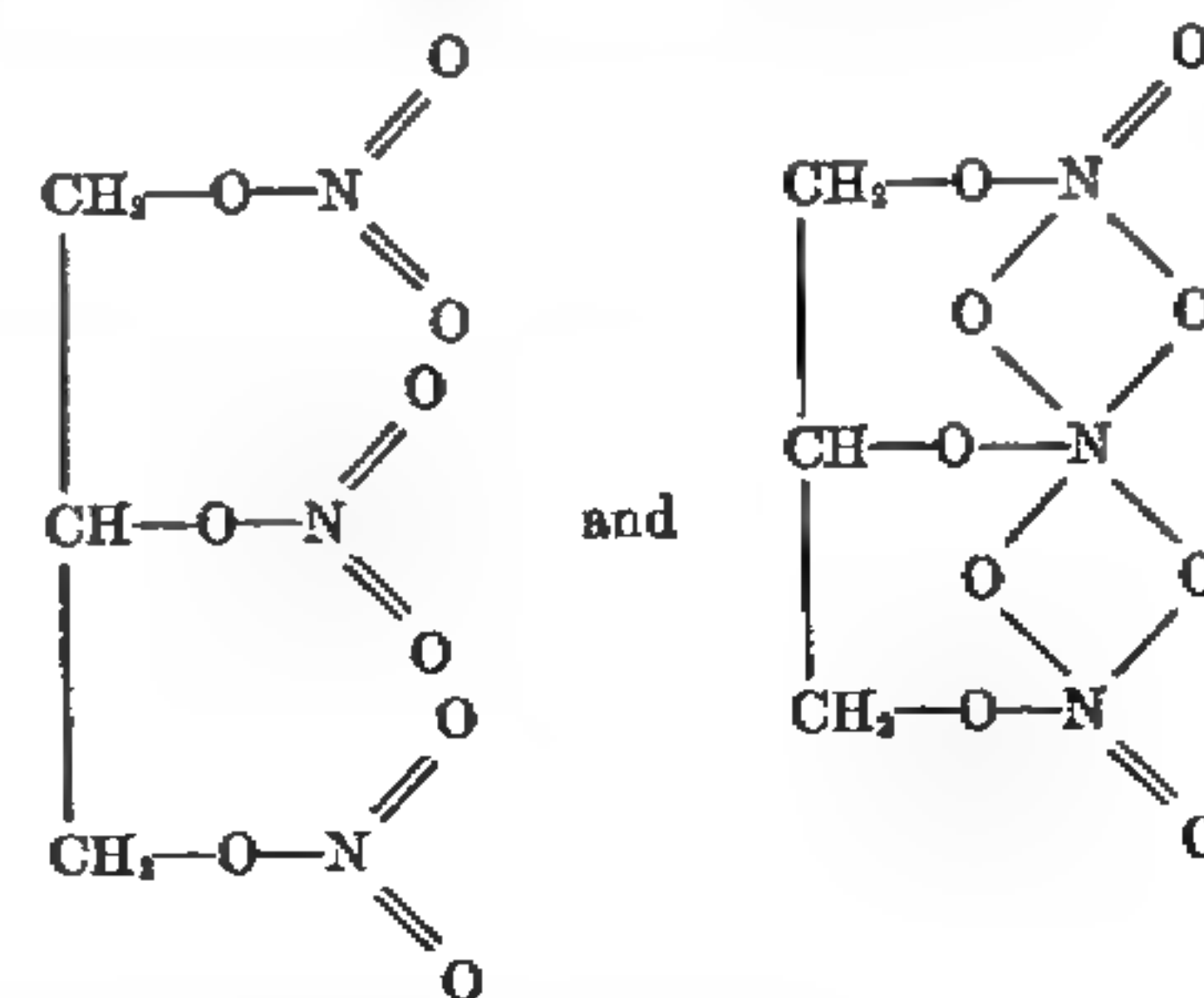
Hibbert¹¹ specifies the following test conditions to obtain the labile or stabile isomers with certainty: If freshly prepared nitroglycerine, which has not been frozen, is mixed with wood meal, cotton, powdered glass wool, or powdered stoneware, preferably powdered glass wool, and the mixture stirred vigorously and cooled to -40°C . the labile isomer is always formed. Another sample of the nitroglycerine is seeded with a small quantity of the frozen product, likewise stirred, whereupon the nitroglycerine crystallizes in the labile form.

If, on the other hand, it is mixed with wood meal and powdered sodium nitrate, the stabile isomer is formed under otherwise similar conditions. Nitroglycerine once frozen gives sometimes the labile, sometimes the stabile form with wood meal. As far as the former is formed, it goes readily over into the stabile form, for example by vigorous stirring with a glass rod. If the previously frozen product is mixed with wood meal and sodium nitrate the stabile form always occurs. Ammonium nitrate acts like sodium nitrate. On the other hand, potassium nitrate has no effect in this connection.

¹¹ Z. Schiess- u. Sprengstoffw. (1914), p. 83.

Hibbert¹² gives exact observations on the conditions of conversion of the isomers. According to him, any nitroglycerine crystallizes in the form with which it is seeded. The crystallized, labile isomer can be preserved for a long time, one or two weeks, without change, but the crystals gradually lose their transparency and pass over into the stabile form. The latter can never be converted into the labile form again without passing through the liquid phase. If the nitroglycerine has previously been frozen in the stabile form, and after melting frozen in the labile form by seeding, the conversion takes place readily. In general a vigorous stirring suffices for this, for example with a glass rod at -20 to -60°C . Occasionally the change occurs without apparent cause. If the labile crystals are stirred in contact with a stabile crystal at 2 to 4°C . the conversion of the whole mass takes place within thirty to forty seconds with a 10° rise in temperature.

Both isomers, when melted and heated for a short time to 20 to 30°C ., on cooling crystallize spontaneously again in the original form, so that it must be assumed that both forms also exist in the liquid state. These facts led Hibbert to suspect¹³ that possibly it is not only a question of physical but also chemical isomerism, as is conceivable by the following structural formulae:



¹² Z. Schiess- u. Sprengstoffw. (1914), p. 126.

¹³ Z. Schiess- u. Sprengstoffw. (1914), pp. 306 and 321. See also Nauckhoff's Investigations.

Up to the present there is no proof in this connection seems to have been brought forward as regards any different behaviour of the two liquid forms, either chemically or physically, e.g., solubility.

Crystal form. The crystal form of the stable isomer has been determined by Fack¹ and of the unstable form by Habert.² The former belongs to the diprismatic class, the latter to the triclinic system, see plates.

Specific heat, latent heat of fusion, heat of conversion. These physical constants have been determined by various authors, at first in part by Beckertinn,³ later by Nauckhoff⁴ and finally by Habert and Fuler.⁵ The specific heat of liquid nitroglycerine is given by Nauckhoff as 0.356 calories per second and as 0.315 cal./sec. The heat of conversion of the isomers was determined by Habert and Fuler, together with the heat of crystallization and latent heat of fusion, after overcoming great experimental difficulties, partly due to the slowness of the crystallization, by means of the Bunsen ice calorimeter as 280 calories per gram. The following heat evolutions were obtained:

	$\frac{t}{\text{sec.}}$	$\frac{d}{\text{cal./sec.}}$
1. Liquid phase \rightarrow stable solid phase	5.2	1194.4
2. Liquid phase \rightarrow unstable solid phase	28.0	636.0
3. Liquid phase \rightarrow stable, solid phase	33.2	7536.4

The theory of the freezing point depression of nitroglycerine, as well as the action, reaction at the freezing point by vapourization and by crystallization, is treated in the introduction of the chapter on Nitroglycerine Dynamics.

Solubility relations.

Nitroglycerine is characterized by high solubility in most organic solvents, and, in view of being itself an extraordinarily good solvent

¹ *Z. Schmelze u. Sprünge*, 1911, p. 124.

² *Z. Schmelze u. Sprünge*, 1911, p. 4, pp. 87 and 176.

³ *S. Langbein u. A. Langbein*, *J. Prakt. Chem.*, 1877, 2, 59 etc.

⁴ *Z. anorg. Chem.*, 1905, pp. 11 and 13. *Z. Schmelze u. Sprünge*, 1911, I, p. 174.

⁵ *Z. Schmelze u. Sprünge*, 1911, p. 4, pp. 273 and 296.

⁶ For the right signs determined by the authors the values of 280 and 244 cal. in the literature are often inaccurate.

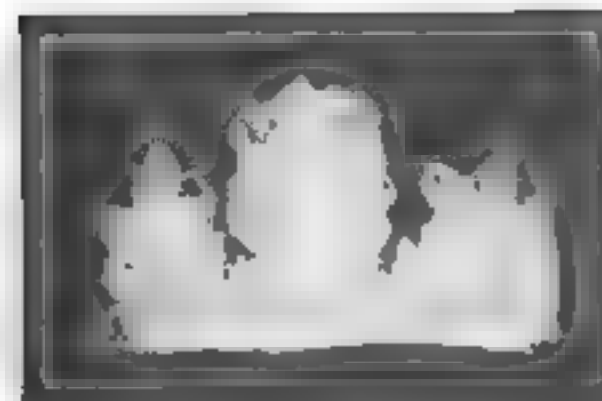


FIG. 22. STABLE ISOMER

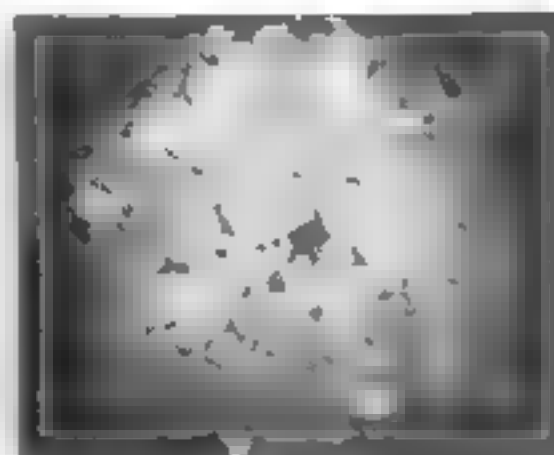
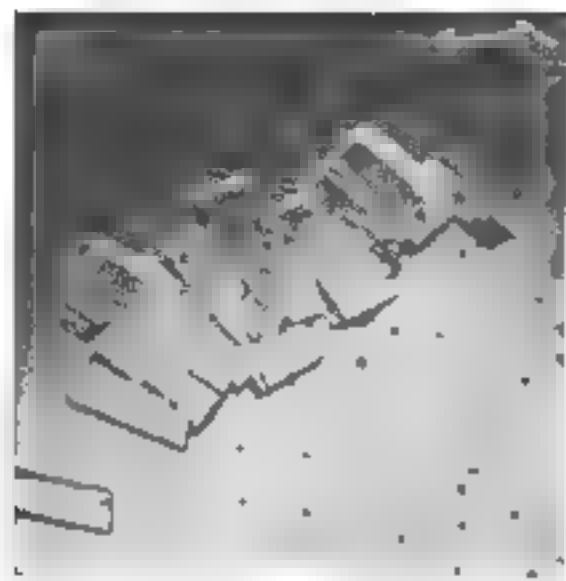


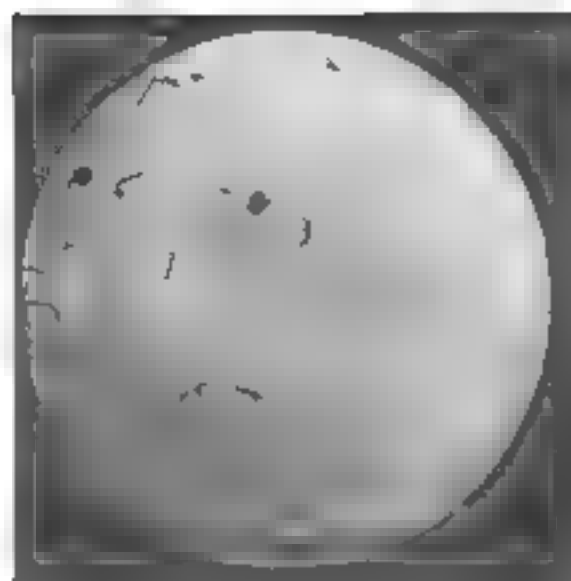
FIG. 23. UNSTABLE ISOMER



FIG. 24. NITROGLYCERINE CRYSTALS STABLE ISOMER (FROM LANGBEIN)³
NATURAL SIZE



I



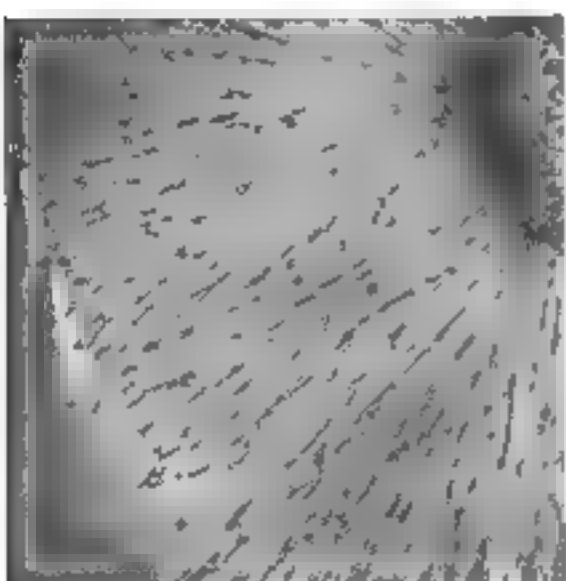
II



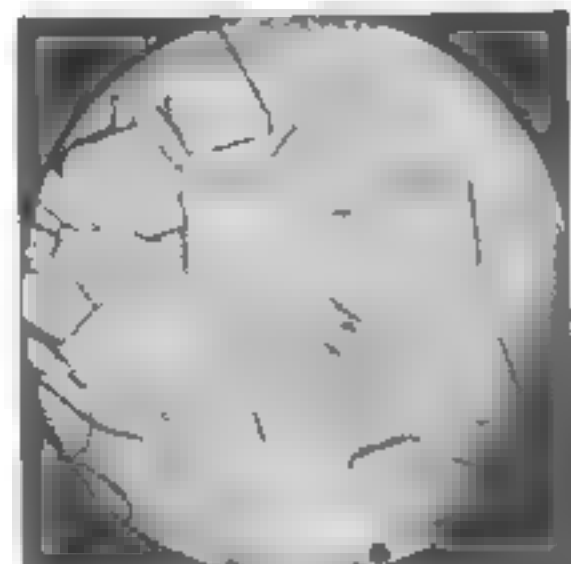
III



IV

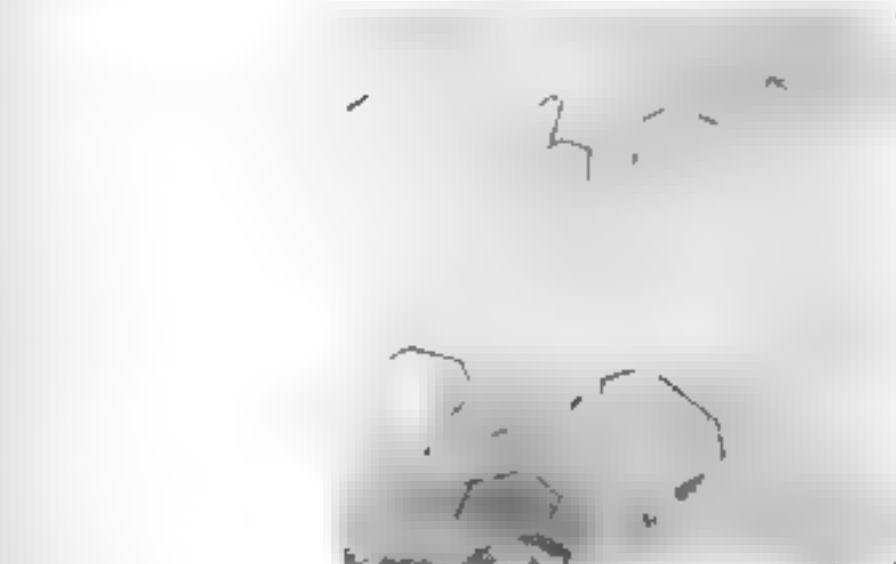


V



VI

FIG. 237. NITROGENOUS CRYSTALS. (HODGKIN)



VII

FIG. 238. NITROGENOUS CRYSTALS. (HODGKIN)

These relations mean solubility in all proportions in many of the known solvents. Nitroglycerine is miscible in all proportions at ordinary temperatures with the following liquids:

Methyl alcohol	Pyridine
Acetone	Nitrobenzene
Ether	Nitrotoluene
Ethyl acetate	Liquid dinitrotoluene
Amyl acetate	Chloroform
Glacial acetic acid	Ethylene chloride
Benzene	Ethylene bromide
Toluene	Dichloroethylene
Xylene	Tetrachloroethane
Phenol	

In aqueous acetic acid its solubility depends upon the concentration, being appreciable in 65 per cent acid, for example, making possible a separation from nitrocompounds (see Explosive Analysis, Supplement).

Certain highly substituted chlorine hydrocarbons behave differently from the above chlorine compounds, for example, 100 parts of trichloroethylene dissolve only 20 parts of nitroglycerine, 100 cc. of carbon tetrachloride only 2 cc.; perchloroethylene and pentachloroethane dissolve very little.

The ready solubility in ether, chloroform and dichloroethylene is of great importance in the extraction of nitroglycerine from smokeless powder and explosive mixtures, on account of the low boiling point of these solvents and the non-flammability of the last two.

It is likewise miscible in all proportions with the homologous and related nitric esters, such as:

Methyl nitrate	Trimethylene glycol dinitrate
Ethyl nitrate	Dinitrochlorohydrine
Nitroglycol	Acetyldinitroglycerine
Dinitroglycerine	Tetranitrodiglycerine, etc.

Mixtures with nitroglycol, dinitroglycerine, dinitrochlorohydrine and tetranitrodiglycerine come into consideration as practically non-freezing oils.

Ethyl alcohol occupies a peculiar position, since its solvent power varies greatly with the temperature and water content. Even absolute alcohol dissolves only a limited amount at ordinary temperatures, while hot alcohol mixes with nitroglycerine in all proportions. The solubility in alcohol gradually falls with the degree of dilution of the latter, so that it is very slightly soluble in 50 per cent alcohol, and

can be almost completely precipitated from the alcoholic solution by the addition of water.

Propyl, isopropyl and amyl alcohols act similarly, likewise dissolving nitroglycerine at ordinary temperatures to only a limited degree, but on the other hand at temperatures of the water bath they mix with it in all proportions.

Solubility of nitroglycerine in alcohol

100 cc. absolute alcohol at 0°C. dissolves about 30.0 grams nitroglycerine.

100 grams absolute alcohol at 0°C. dissolves about 37.5 grams nitroglycerine.

100 cc. absolute alcohol at 20°C. dissolves about 43.0 grams nitroglycerine.

100 grams absolute alcohol at 20°C. dissolves about 54.0 grams nitroglycerine.

100 cc. 96 per cent alcohol at 20°C. dissolves about 31.6 grams nitroglycerine.

100 grams 96 per cent alcohol at 20°C. dissolves about 40.0 grams nitroglycerine.

At 20°C. 1 gram nitroglycerine requires for solution 2.3 cc. absolute alcohol.

At 20°C. 1 gram nitroglycerine requires for solution 3.2 cc. 96 per cent alcohol.

At 20°C. 1 cc. nitroglycerine requires for solution 3.7 cc. absolute alcohol.

At 20°C. 1 cc. nitroglycerine requires for solution 5.0 cc. 96 per cent alcohol.

100 cc. 50 per cent alcohol dissolves at 20°C. 1.8 grams nitroglycerine.

100 cc. 25 per cent alcohol dissolves at 20°C. 0.7 grams nitroglycerine.

On dilution of the saturated nitroglycerine solution in 50 per cent alcohol there is therefore a separation. On further dilution of the solution in 25 per cent alcohol there is no separation. Dilution curves and solubility curves are parallel.

Even at about 50°C. nitroglycerine mixes with 96 per cent alcohol in all proportions. On the other hand, at 20°C. nitroglycerine dissolves only 5.4 per cent alcohol, and at 0°C. only 3.4 per cent.

Nitroglycerine is only slightly soluble in carbon disulphide, which is important in the separation of nitrocompounds when analyzing explosives, the latter being soluble in this solvent.

At ordinary temperatures 100 cc. of carbon disulphide dissolves 1.25 grams of nitroglycerine, but on the other hand, 100 grams of nitroglycerine dissolves 2.5 grams of carbon disulphide.

Nitroglycerine is almost insoluble in glycerine at ordinary temperatures, and is only very slightly soluble on heating. The simplest divalent alcohol, glycol, assumes an intermediate position between ethyl alcohol and the trivalent alcohol glycerine as regards solvent powers, since it dissolves nitroglycerine to a certain extent, 100 parts of glycol at 20°C. dissolving 12 parts, and at 80°C. 20 parts of nitroglycerine.

Contrary to older statements nitroglycerine is not wholly insoluble, but only slightly soluble at ordinary temperatures, and even less soluble on heating, in the light and heavy mineral oils consisting mainly of paraffin hydrocarbons like benzine, ligroin, petroleum, paraffin oil and vaseline oil, but more readily soluble on the other hand in fatty oils, e.g., in castor oil, in 4 parts of olive oil at 100°C., in 5 parts at 20°C., in 5 parts of rapeseed oil at 100°C., and 7 parts at 20°C.

100 grams ligroin at 20°C. dissolves about 1.5 grams, at 80° about 6 grams nitroglycerine.

100 grams petroleum at 20°C. dissolves about 2 grams, at 80° about 6 grams nitroglycerine.

100 grams paraffin oil at 20°C. dissolves about 4 grams, at 80° about 9 grams nitroglycerine.

Solubility in water. Nitroglycerine is very slightly soluble in water, although not completely insoluble, and consideration should be taken of this fact in yield determinations, to avoid injuring the yield by washing with too large quantities of water.

According to Will:²⁰ 1 liter water at 15° dissolves 1.6 grams nitroglycerine.

According to the author's tests 1 liter water at 20° dissolves 1.8 grams nitroglycerine.

According to the author's tests 1 liter water at 50° dissolves 2.5 grams nitroglycerine.

Solubility in alkalis and acids. In cold sodium hydroxide or potassium hydroxide solutions, or in ammonium hydroxide nitroglycerine is insoluble, but on heating gradual solution occurs with saponification.

Concentrated sulphuric acid dissolves nitroglycerine easily, split-

²⁰ Z. Schiess- u. Sprengstoffw. (1908), p. 373.

ting off HNO_3 , and depending upon the conditions of concentration there can be decomposition to the lower nitrates or even to glycerine sulphate. One hundred grams of 98 per cent sulphuric acid at 20°C . dissolves about 26 grams of nitroglycerine.²¹ Then the HNO_3 set free, which at certain concentrations tends to form nitroglycerine again, leads to a state of equilibrium, and no further quantities of nitroglycerine dissolve.

Nathan and Rintoul²² have made exhaustive studies on the solubility of nitroglycerine in mixed acids of various compositions and the equilibrium conditions between such mixed acids, nitroglycerine and glycerine sulphate (see also under Operating Results).

At ordinary temperatures the very strongest nitric acid, specific gravity 1.5, mixes with nitroglycerine in all proportions. Its solvent powers decrease with increasing water content. Nitric acid containing 65 per cent HNO_3 , specific gravity 1.4, at 20°C . dissolves about 8 grams of nitroglycerine per 100 grams of the acid. Solutions of nitroglycerine in nitric acid undergo rapid decomposition on standing, with oxidation and evolution of nitrous acid.

Nitroglycerine is insoluble in cold, concentrated hydrochloric acid. On heating there is a gradual decomposition, with formation of a dark yellow color and development of nitrosyl chloride.

Solvent powers for nitrocompounds. There still remain to be mentioned the appreciable solvent powers of nitroglycerine for the nitrocompounds of the aromatic series, especially when warm, because this is important in the manufacture of plastic and gelatinous explosives, since the nitrocompounds, just like nitroglycerine, gelatinize nitrocellulose. For example, dinitrotoluene and trinitrotoluene, when warm, mix with nitroglycerine in all proportions to a clear melt. A fusion of equal parts of nitroglycerine and pure 2,4,6-trinitrotoluene is still liquid at about 60°C . On cooling the solution or eutectic mixture the nitrocompound in part crystallizes out, showing a tendency to supercool.

100 grams of nitroglycerine at 20°C . holds 35 grams of dinitrotoluene in solution.

100 grams of nitroglycerine at 20°C . holds 30 grams of trinitrotoluene in solution.

²¹ 100 grams of 70 to 80 per cent sulphuric acid dissolve only about 7.5 grams nitroglycerine.

²² *J. S. C. I.* (1908), vol. 27, p. 143.

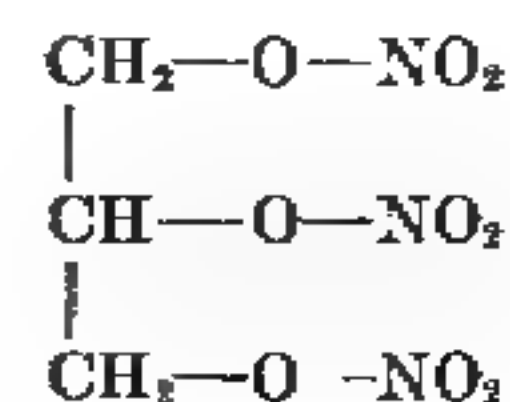
Solubility powers for nitrocellulose (gelatinizing powers). Nitroglycerine has a very appreciable solvent action on certain kinds of nitrocellulose, which are designated as collodion nitrocotton or soluble nitrocellulose. It dissolves them on long standing of the mixture at ordinary temperatures, or after a short time, e.g., fifteen to twenty minutes, at higher temperatures such as 60 to 65°C ., to a more or less stiff colloid, depending upon the concentration of the solution. For example, 100 parts of nitroglycerine, even with 2.5 parts of collodion nitrocotton, form an elastic, non-leaking colloid, which can be cut and which will retain its shape at ordinary temperatures. The quality of the collodion nitrocotton determines the quantity of the latter required, or the proportion of collodion nitrocotton present. This is called its "gelatinizing power." Aromatic nitrocompounds or substituted ureas (centralite) dissolved in the nitroglycerine promote the colloid formation. This property of nitroglycerine, discovered by Nobel, is important in the manufacture of plastic (gelatine) explosives, blasting gelatine and smokeless powder.

A summary of the solvents for nitroglycerine, approximately corresponding to the above more accurate data, is found in Guttman, *Industrie der Explosivstoffe*, page 437, and Escales, *Nitroglycerin und Dynamit*, p. 133.

CHEMICAL PROPERTIES

Chemical investigation; stability, and decomposition

Nitroglycerine shows the chemical nature of an ester. On reduction, for example with tin and hydrochloric acid, glycerine is regenerated, while on reduction of a true nitrocompound, for example nitromethane or nitrobenzene, the corresponding amide compounds, methylamine and aniline, are formed. It therefore contains no nitrogen atoms directly attached to carbon atoms, and is formed by condensation and not by substitution. Its structural formula is therefore:



and, as mentioned in the introduction, the designation of nitroglycerine is improper and has only the value of an adopted and deep-rooted abbreviation. The proper designation is glycerine trinitrate or the trinitric ester of glycerine. Therefore it is saponified by alkalies, particularly easily by alcoholic potassium or sodium hydroxide, wherein the glycerine is partly converted into organic acids by oxidation, while on the other hand nitrite is formed in addition to sodium nitrate. According to Hay²³ the saponification with alkalies is according to the following equation:



However, this equation does not embrace all the processes in the reaction because other products, such as aldehyde resin, oxalic acid and ammonia have been observed.²⁴

In the alkaline saponification glycerine does not appear as the product of the saponification.²⁵ If the saponification is by caustic alkali in the presence of phenyl mercaptan, glycerine appears as the product of the saponification and the phenyl mercaptan is converted into diphenyl sulphide.²⁶

Alkali sulphides are still more powerful saponifying agents, K_2S , KHS and CaS reforming glycerine.²⁷

Hydroiodic acid of specific gravity 1.5 decomposes nitroglycerine into glycerine and nitric oxide.²⁸

According to Häussermann²⁹ nitric oxide in the form of ammonia is split off on reduction with zinc and acetic acid.

Nitroglycerine dissolves readily in concentrated sulphuric acid, splitting off nitric acid, which latter becomes evident by the fuming of the acid. Under certain conditions there can be decomposition to glycerine sulphate, i.e., an acid saponification.

²³ *Monit. Scient.*, vol. 15, p. 424, and *Jahresber.* (1885), p. 1173.

²⁴ Regarding the alkali saponification see also Vignon and Bay, *Bull. soc. chim. -biol.* (3), vol. 29, p. 26 (1903); *C. R.*, vol. 135, p. 507 (1902); Silberrad and Farner, *J. Chem. Soc.*, vol. 89, p. 1759 (1906); Berl and Delpy, *Ber.*, vol. 43, p. 1421 (1901) and other literature.

²⁵ Carlson, *Ber.*, vol. 40, p. 4192.

²⁶ Klason, Carlson: *Ber.*, vol. 39, p. 2753, C. 1907, II, p. 1226.

²⁷ *Jahresber.* (1883), p. 858; *Chem. News*, vol. 47, p. 169 (1883).

²⁸ Mills, *Jahresber.* (1864), p. 494; *J. Chem. Soc.*, vol. 17, p. 153 (1864).

²⁹ Further chemical action: MacDonald, *Arms and Explosives* (1908), April and May; *Z. Schiess- u. Sprengstoffw.* (1908), p. 425.

Chemical decomposition of nitroglycerine leads first to the lower degrees of nitration, mainly dinitroglycerine. German patent 175751 (1904) discloses a method of preparation of dinitroglycerine based upon this reaction.

When nitric acid acts upon nitroglycerine for a longer period, or more rapidly at higher temperatures, there is a complete decomposition with evolution of nitrous vapors and formation of an acid syrup composed of oxidation products, among them glyceric acid (see also chapter on Stability).

Chemical tests

1. *Determination of moisture.* Nitroglycerine manufactured on a commercial scale is slightly turbid when fresh, on account of a 0.4 to 0.6 per cent moisture content. It is not hygroscopic, and has very slight solvent power for water. Clear nitroglycerine can contain at most 0.1 to 0.2 per cent moisture.

This moisture is determined by drying nitroglycerine, spread out in a thin layer in a calcium chloride desiccator, until constant weight is obtained. Also a short period of heating in a shallow, open dish at 40 to 45°C. gives sufficiently accurate results.

2. *Acidity and alkalinity.* Before using, nitroglycerine must be absolutely neutral, and should contain neither traces of acid nor free alkali. The former causes gradual decomposition on standing. The latter, which may be due to unextracted sodium carbonate, can be a source of deception in the stability test, because it gives a higher stability than is actually the case. An excess of sodium carbonate can conceal unextracted traces of acid still present, and can even act as a saponifying agent. For this reason the sample is shaken vigorously with distilled water, separated in a funnel, and the water tested by methyl orange or Congo Red. If necessary, the alkali can be titrated by 0.1 N acid.

3. *Chemical analysis.* Determination of the nitrogen content is usually employed in deciding the chemical purity. The nitrogen content of commercial nitroglycerine is about 18.40 per cent, but with chemically pure, water-white and clear nitroglycerine the theoretical figure of 18.50 per cent, or within the experimental analytical error of 18.48 to 18.52 per cent, is always found.

The nitrogen can be determined by various methods. The most simple and undoubtedly the most reliable is the decomposition with

sulphuric acid, reduction by mercury, and volumetric determination of the evolved nitric oxide by a Lunge nitrometer, as is quite customary in all explosives plants. A description and method of operation of this apparatus is given under Nitric Acid Analysis. The method of use here does not differ appreciably from that in the analysis of mixed acid. Lunge himself describes the determination of nitrogen in nitroglycerine by means of the nitrometer in *Dingler's Polytechnischen Journal*, volume 245, page 171. Hess³⁰ and W. Hempel³¹ also used this method for nitroglycerine.

Hess weighed out a small quantity of nitroglycerine, e.g., 0.12 gram, in a glass weighing bottle, dissolved it in concentrated sulphuric acid, poured the solution into the upper bowl of the nitrometer, washing out the weighing bottle first with concentrated and then rather dilute sulphuric acid of about 2 parts of acid to 1 of water. Since the weighing bottle and the upper part of the bowl of the nitrometer must be washed out quantitatively, which means several times, in order to wash the nitroglycerine solution completely into the reaction bulb, too much sulphuric acid was consumed and had to be corrected for. Moreover, the method is somewhat inconvenient and small losses can be caused by splashing and fuming of the nitric acid present. It is simpler to allow the required amount of nitroglycerine to drop out of a weighing pipette, weighed both before and after, into the upper bowl of the nitrometer, suck in the main quantity by a slight negative pressure, and quickly add sulphuric acid, which can likewise be rapidly sucked in by a quick and careful opening and closing of the stopcock, so that the last few drops of nitroglycerine which rapidly float to the surface, will be sucked in with it. Repeating this operation twice transfers the nitroglycerine completely to the reaction bulb. The washing can also be done with a somewhat weak and consequently lighter sulphuric acid, in which the nitroglycerine sinks. If the measuring tube is graduated from 100 to 150 cc., and the reaction bulb is 100 cc., a sample of 0.38 to 0.42 gram is weighed out.

If mixtures of nitroglycerine and mononitrocompounds, such as mononitronaphthalene or other easily nitrated substances like centralite, are to be analyzed, as may happen in the analysis of explosives or double base smokeless powders which have undergone extraction, this method of determining the quantity of nitroglycerine present is no longer applicable, because these compounds are immediately partially or further nitrated by the nitric acid split off from the nitroglycerine by the sulphuric acid, and a part of the nitrogen which would otherwise appear as NO is removed and too little nitroglycerine found. Nitro groups are not split off by mercury and sulphuric acid. On the other hand, the method is applicable to mixtures of nitroglycerine and di- or trinitrotoluene, because at ordinary temperatures these do not absorb nitric acid.

³⁰ *Mitt. Art.-u. Geniewesen* (1881), Notizen, p. 137.

³¹ *Z. f. analyt. Chem.*, vol. 20, p. 82, and vol. 26, p. 312.

Three factors cause the nitrometer in its simplest form to be somewhat time consuming and inconvenient. The mercury and the glass walls warm up considerably from the heat of reaction, so that after shaking there must be a wait of fifteen to twenty minutes before reading, to give equalization of temperatures. Adjustment to atmospheric pressure, which cannot be done by a simple leveling of the liquids in both bulbs on account of the presence of the sulphuric acid, is inconvenient, requires some practice, and may necessitate repeating the analysis because of loss of gas. Finally the sulphuric acid occasionally forms foam or bubbles, and does not allow the meniscus to be read easily. For this reason it is often recommended that gas development be conducted in a simple shaking bulb outside of the nitrometer itself and having no graduations, and the gas then transferred into a mercury burette without the sulphuric acid accompanying it, so that reading can be done easily after ten minutes by merely adjusting the level tube.

Hempel developed a special and somewhat complicated apparatus for this process, which is applicable to all nitric esters, but which can be replaced by a simple nitrometer in connection with a mercury burette.³²

Determination of nitrogen by reduction with ferrous sulphate in acid solution

1. Hess method: Boiling with ferrous sulphate in sulphuric acid solution.

F. Hess³³ developed a method for the liquid or volatile nitric esters, which is an adaptation of the Champion and Pellet method,³⁴ also called the Schultze-Tiemann method, for the determination of nitrogen in nitrocellulose by boiling with ferrous chloride and hydrochloric acid. This latter method cannot be used for volatile nitric esters. The essential difference from the older methods is that the liquid nitric esters are not put into the boiling flask at first, and are not present during the boiling out of the air, because of their volatility, but instead the flask is at first boiled air-free with a solution of 20 to 25 grams of ferrous sulphate in about 100 cc. of distilled water, and then after cooling the quantity of nitroglycerine to be analyzed, dissolved in concentrated sulphuric acid, is carefully sucked in by reduced pressure and washed in quantitatively, first with strong, then with weaker sulphuric acid, and finally with water. The rest of the operation is the same as in the nitrogen determination of nitrocellulose by ferrous chloride and hydrochloric acid. After most of the water has boiled off and a certain concentration has been obtained, it must without fail be again cooled and 20 to 25 cc. of water added to insure all of the nitric oxide being set free. By using this method Hess obtained almost theoretical values,

³³ *Z. f. analyt. Chem.*, vol. 20, p. 82, and vol. 26, p. 312. *Escales: Nitroglycerin und Dynamit*, p. 144.

³⁴ *Mitt. Art.-u. Geniewesen* (1888), Notizen, p. 139. See also *Escales: Nitroglycerin und Dynamit*, p. 145.

³⁵ *C. R.*, 83, 707.

namely 18.42 to 18.55 per cent N., the theoretical being 18.50 per cent. In general this method has hardly any advantages over the nitrometer method.

2. *Wolff process: Decomposition with ferrous chloride and hydrochloric acid in a current of carbon dioxide.* C. H. Wolff³⁵ drives out the air from the reaction flask by means of a current of carbon dioxide instead of steam, and so avoids the inconvenience attending the handling of apparatus at positive and negative pressures.

The weighed sample of nitroglycerine is placed in a decomposition flask holding about 50 cc., and 5 to 10 cc. of a mixture of previously boiled and cooled concentrated ferrous chloride solution, and concentrated hydrochloric acid is added. The flask is then closed, and a current of carbon dioxide from a generator passed through it to drive out the air. When the gas bubbles passing from the gas delivery tube to the measuring tube are completely absorbed by the 20 per cent sodium hydroxide solution in the measuring tube the current of carbon dioxide is cut off and the flask very gradually heated by a small gas flame to start the decomposition of the nitroglycerine and the formation of nitric oxide. When the decomposition is finished the flask is heated more strongly and finally boiled until only a few cubic centimeters remain. Finally the last traces of nitric oxide are swept into the measuring tube by again passing carbon dioxide through the system.

For the sake of completeness the following methods of analysis should also be mentioned:

The nitrogen in nitroglycerine can also be converted into nitric acid and the latter titrated or determined gravimetrically, e.g., by nitron.

Hampe³⁶ decomposes nitroglycerine by means of concentrated sulphuric acid and mercury, converts the compounds of nitrogen and oxygen which have been formed into nitric acid by oxygen and hydrogen peroxide, and determines the latter by titration.

It would be simpler to convert the nitric acid of the nitroglycerine into a mixture of nitrate and nitrite by saponification with alkali in the presence of hydrogen peroxide, so that on acidifying in the presence of hydrogen peroxide the nitrite would be converted completely to nitrate, and the latter determined gravimetrically by nitron. See the corresponding Busch and Schneider method for nitrocellulose, *Z. Schiess- und Sprengstoffwesen* (1906), page 232.

³⁵ *Repertor. d. analyt. Chem.* (1881), No. 13; see also Escales, *Nitroglycerin und Dynamit*, p. 147.

³⁶ *Z. Berg-, Hütten-, Sal.-Wes.*, vol. 31.

Silberrad, Phillips and Merrimann³⁷ saponify the nitroglycerine by heating it for six hours with sodium hydroxide solution in a reflux condenser. An aliquot part of the product of saponification is reduced to ammonia by two parts of zinc powder and one part of Ferrium Reductum in 40 per cent sodium hydroxide, and the ammonia evolved determined in the usual way by absorption in 0.1 N acid. They obtain 18.39 to 18.53 per cent N., the theoretical being 18.50 per cent.

Chemical stability; stability tests; decomposition of nitroglycerine

Absolutely pure nitroglycerine, completely free from any trace of acid, is from a chemical point of view and under ordinary conditions an absolutely stable compound, in spite of the quantity of energy slumbering in it and the easy release of the internal tension of the molecule by friction, blows between hard objects or sudden heating. At ordinary temperatures it remains unchanged for an unlimited time, as far as has been observed. Even diffuse daylight does not seem to affect it, since various samples have been preserved in laboratories for years without change. It is said that at the Avigliana plant in Italy samples of nitroglycerine are still preserved today which were made by its discoverer Sobrero, and are therefore more than seventy years old, which is a surprising stability considering the means then available. Some years ago in Sweden a shaft containing forgotten boreholes loaded with nitroglycerine and apparently thirty-eight years old was discovered, dating from a time when liquid nitroglycerine was still used as an explosive. The latter had remained unchanged, perhaps in a frozen condition because at a temperature of about 8°C., summer and winter. On detonating its full strength was developed.³⁸

Moreover, heating to moderate temperatures prevalent in hot countries causes no chemical change in nitroglycerine for long periods. Plants exporting to Africa have retained samples of blasting gelatine and gelatine dynamite which have passed through the equator twice and been subjected to the African climate for several years without chemical change and without showing traces of acidity. The molecule tends to undergo chemical decomposition and split off free nitric

³⁷ *J. S. C. I.*, vol. 25, p. 628.

³⁸ *Z. Schiess- u. Sprengstoffw.* (1913), p. 199.

acid and later nitrous acid only after long-continued action of temperatures around 50°C. and up.

This decomposition takes place gradually even at ordinary temperatures, and more rapidly the higher the temperature, provided that in manufacture and purification the last traces of free acid have not been removed by neutralization. If the nitroglycerine is sealed up so that the first traces of decomposition products cannot escape, the latter act as catalysts in the sense of favoring the decomposition, i.e., an acid saponification with oxidation.

Although the reaction is exothermic, it proceeds to the end without danger when only small quantities are involved. At ordinary temperatures acid nitroglycerine samples give up all of their nitrogen in the form of nitrous vapors very slowly in the course of many days, but at higher temperatures correspondingly faster, leaving finally a strongly acid, thick syrup containing glyceric acid and other oxidation products. On slow decomposition without rise of temperature 10 parts of nitroglycerine finally form about 4.3 parts of a white crystal soup containing about 2 parts of oxalic acid, in addition to other acids and oxidation products.

When large quantities of enclosed nitroglycerine become acid such a process of decomposition can, by accumulation of slowly developed heat, accelerate to a dangerous degree and lead to explosion.

The complete removal of acid from nitroglycerine down to the very last traces is therefore an indispensable requirement for the manufacture of useful, commercial material.

Stability tests. Various tests serve to determine the fulfillment of this condition. The best known and the most used, because the most rapid although not the most reliable, is the so-called Abel heat test.

This method, first used by Abel, an Englishman, depends upon the exceedingly sensitive reaction of potassium iodide-starch with very small traces of nitrous acid. From the time of its preparation nitroglycerine contains dissolved nitric and nitrous acids, the last traces of which can only be removed by intensive and persistent washing with alkaline liquids at high temperatures. If this purification process is insufficient, heating the nitroglycerine sample to 70 to 80°C. soon evolves traces of nitrous acid or the like from decomposition of the nitric acid, coloring blue a moistened piece of paper impregnated with potassium iodide-starch mixture suspended above it. On long

heating even completely purified nitroglycerine gradually splits off small traces of nitrous acid at the above temperatures, which become evident by the separation of iodine in the extremely sensitive reagent. The time up to the appearance of, and the degree of the reaction, measure the stability of the nitroglycerine sample.

To make this test an apparatus like that shown in figure 24 is constructed. There is necessary:

1. A cylindrical or hemispherical water bath of glass or 1 mm. copper sheet, filled with water to within 1 cm. of the top. The cover, likewise of sheet copper, has an overhanging rim which keeps it in place. The cover has a

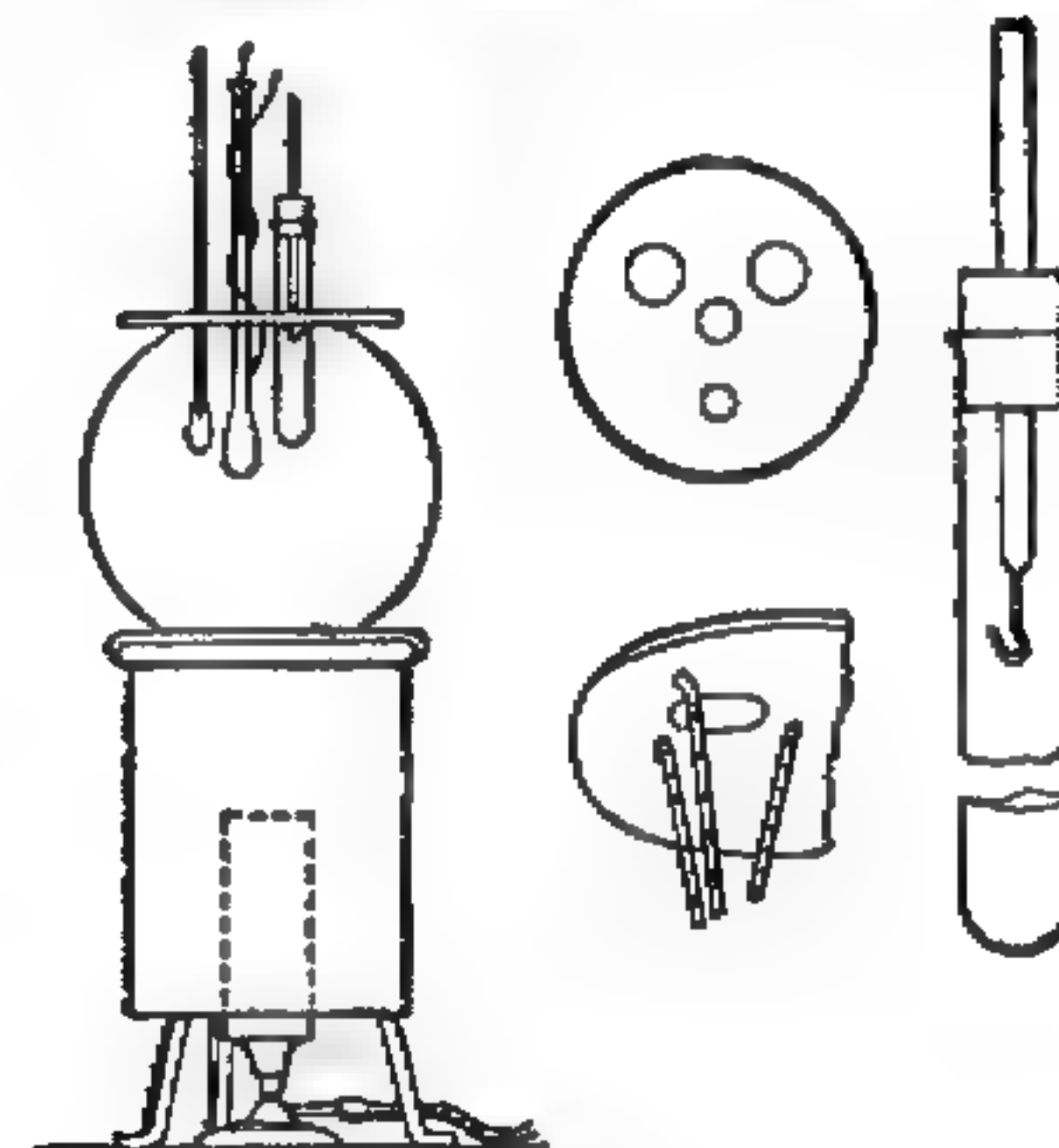


FIG. 24. ABEL HEAT TEST APPARATUS

number of circular openings 20 mm. in diameter, one of which holds a perforated stopper and a Centigrade thermometer which extends about 10 cm. into the water. The others are provided with springs made of sheet metal to hold the test tubes with the samples in the desired position.

2. Test tubes of suitable width, for example 16 to 20 mm., and 14 to 15 cm. high, not too thin-walled, so as not to break too easily. The latter are closed by rubber stoppers, through which glass rods extend. At the lower end of these glass rods a short piece of approximately 0.5 mm. platinum wire is melted on, forming at the bottom a hook to hold the test paper.

3. Potassium iodide-starch paper or zinc iodide-starch paper. The latter is even more sensitive than the former, and is used in testing nitroglycerine intended for the manufacture of smokeless double base powder. According to an old English prescription the potassium iodide-starch paper is made as follows:

White starch, 2.7 grams, is washed with water and agitated with 250 cc. of distilled water, brought to boiling and boiled gently for ten minutes. The

colloidal solution obtained is intimately mixed with a solution of 0.9 gram of potassium iodide, freshly recrystallized from alcohol, in 250 cc. of distilled water. Strips of white, not too thick filter paper, washed with water, are immersed for ten seconds in the above solution, then hung on threads in a dark, dust- and acid-free room to drain and dry. The dried paper is cut into strips 30 mm. long and 10 mm. wide, which are preserved in well stoppered bottles of dark glass, because the paper is sensitive to light, particularly when moist. The sensitiveness of the reagent paper tends to diminish in the course of time, so that after a few months the unconsumed supplies should be replaced by fresh stock.

4. Glycerine solution. Moist test paper is much more sensitive than the dry. To moisten it with water would be useless because the strips would soon dry over the warm test bath. For this reason a 40 to 50 per cent glycerine solution, made of pure glycerine and distilled water and stored in a flask whose perforated stopper has a hair brush or a glass rod constricted at the end, is used. With either of these a line is drawn across the center of the test paper, and by absorption this line soon becomes broader. The coloration appears at the line between the dry and the moist parts of the paper, showing the occurrence of the reaction.

On account of the exceedingly high sensitiveness of the stability test it must be done in a room absolutely free from acid vapors. For this reason explosives and powder plants or their laboratories have special rooms in which no other chemical work is done, and which are suitably separated from the other rooms. The apparatus is set up near a window, in order to be able to clearly observe the reaction, but it should never be in direct sunlight because this also gives the reaction. For example zinc iodide-starch paper is so sensitive that in bright sunlight a brown color shows up in one minute.

The water bath is then heated to 72°C., or when testing nitroglycerine for use in smokeless powder to 82°C., and held at this point by an adjustable burner, so that the temperature variations will be less than 1°. The nitroglycerine sample is allowed to drop into the test tube through a small paper filter until it reaches a mark corresponding to 3.2 grams or 2 cc. Small variations in this do not affect the result. The filtration holds back the last traces of moisture in fresh nitroglycerine samples. Dry, clear nitroglycerine is not filtered. On the other hand, nitroglycerine turbid with moisture must be filtered because the moisture present hinders the reaction and renders the test false. At first the traces of acid formed or already present evaporate with difficulty if the sample contains moisture, and then moisture will precipitate on the upper, cooler walls of the glass tube,

absorbing subsequently evolved traces of acid, preventing the action of the latter upon the test paper.

Since the test papers must not be touched by the hands, because slight impurities such as perspiration can affect them, the papers are placed by tweezers on a large, flat cork stopper, a small hole punched in one end of the papers by a second pair of tweezers, and then they are hung on the bent platinum wire by the hole. The paper is then moistened and placed on the test tube so that it is suspended in about the middle over the sample. After noting the time, the tubes are inserted into the water bath to such a height that the nitroglycerine is at about the same height as the bulb of the thermometer, while the paper strips are above the cover of the water bath.

The test is ended when a light brown line is clearly evident at the line between the dry and the moist parts of the test paper. Formerly a paper of standard color was often used for comparison. This standard paper was prepared by coating strips of paper similar to the test papers with a caramel solution of definite concentration. For further details see Guttman, *Industrie der Explosivstoffe*, Supplement, Heat Test, page 651.

It is usually required that sufficiently purified nitroglycerine stand the heat test for ten or fifteen minutes without showing a coloration of the paper. In England great value is placed on this test, and there, as well as in all the Dominions, nitroglycerine and all explosives containing nitroglycerine are subjected to this test. Also German factories shipping via England or to the Dominions, examine the nitroglycerine for such export explosives in this way, while in domestic (German) manufacture only complete neutrality of the nitroglycerine to litmus is required,³⁹ but the finished explosives must fulfill other stability requirements.⁴⁰

On the other hand, nitroglycerine intended for use in smokeless powder must not color zinc iodide-starch paper inside of twenty minutes at 82°C.⁴¹

The potassium iodide-starch test at 72°C., with thoroughly washed

³⁹ The same is true in the United States.—TRANSLATOR.

⁴⁰ In the United States no stability tests are made on the finished explosives unless they are exported to a country which requires certain tests.—TRANSLATOR.

⁴¹ Only potassium iodide-starch papers are used in the United States.—TRANSLATOR.

nitroglycerine, is usually somewhat longer, e.g., thirty to forty minutes, so that finally only an extremely weak brown line is visible. It is considered suspicious if a clear blue color appears on the paper in a short time, becoming stronger on removing and cooling the tube.

Abnormal phenomena in the Abel test. Several years ago in a large domestic (German) nitroglycerine plant and also in the Ardeer plant of the Nobel Industries Limited, in Scotland, a peculiar thing appeared quite suddenly for a certain period, namely, that nitroglycerine stabilized in the usual manner did not hold up in the Abel test but gave a clear blue color on the potassium iodide-starch paper after only a few minutes. Since the same glycerine, nitrated at the same time in the laboratory with chemically pure acid gave an absolutely normal nitroglycerine, the cause was soon recognized as lying in the commercial mixed acids, and in the further course of the investigation of the nitric acid used in the latter, the nitric acid being made from sodium nitrate by distillation with sulphuric acid. It was found that the first fractions of this nitric acid distillate produced a nitroglycerine which colored the test paper in even 3 minutes.

Finally by great efforts a small quantity of oil was isolated from large quantities of this nitric acid by diluting with water and steam distillation, which on elementary analysis and by its other properties proved to be a mixture consisting mainly of tetranitromethane and chlorotritnitromethane. The vapors of these substances colored the test paper immediately, even if the oil were absolutely free from mineral acids.

The nitric acid contained 0.005 per cent of these organic impurities, which passed over into the nitroglycerine and were strongly retained by it, and naturally could not be removed by washing with water. One gram of this oil, added to 20 kg. of nitroglycerine, reduced the heat test from sixteen to five minutes.

The formation of this mixture of tetranitromethane and chlorotritnitromethane on distillation of nitric acid must be explained by the usual small content of chlorides in the sodium nitrate and also an impurity consisting of traces of organic substances. In the first-mentioned instance of a German plant it could be proved that in the manufacture of the nitric acid some Chile saltpeter had been used which had been damaged in transportation. It had become contaminated by pieces of charcoal during a fire on board ship, and after they were removed it still contained traces of empyreumatic sub-

stances, and tarry bodies, which must be considered as responsible for the formation of the tetranitromethane, etc.

It is known that tetranitromethane is readily formed on heating aromatic bodies with concentrated nitric acid or mixed acid, by splitting the benzene ring. For example, in the nitration of dinitrotoluene to trinitrotoluene traces of tetranitromethane can always be easily recognized by the odor of the crude trinitrotoluene.

The explanation of the incident is due to the tireless work at the Ardeer plant by F. A. Crawford.⁴³

Of more importance than the period of first occurrence of a trace of decomposition is the more or less slow course of the latter. In order to be able to observe this over a long period of time Hess⁴³ described an apparatus and method in which a small quantity of the nitroglycerine to be tested is subjected for a long time to a definite temperature in a porcelain dish in an air bath, and a current of thoroughly purified and dried air passed over it and then into a zinc iodide-starch solution. The appearance of a violet ring at the point where the current of air enters the solution, and the gradual darkening of the solution give a clear picture of the more or less rapid course of decomposition of the sample. Absolutely stable nitroglycerine requires about four hours at 70°C. for the reaction to begin, about ten hours to complete the blue ring, and thirty hours to color the liquid. At 100°C. the decomposition is many times faster, and the above periods then become five, six and ten minutes respectively. Dr. Weeren and Dr. Schellbach have simplified the Hess apparatus.⁴⁴ Escales describes at length an apparatus and method in his *Nitroglycerin und Dynamit* (1908), page 152, and while merely referring to it here it can be said that the daily testing of nitroglycerine in commercial operations by this method is too tiresome and time consuming and for this reason can hardly be used for regular tests.

The usual testing of nitroglycerine and the explosives made from it by the Abel test, as well as the heat test of the latter according to the regulations of the German railroad authorities ensures a sufficient stability of the product. In the Abel test care should be taken to note that no admixed substances, like traces of mercury, are present to mask the test. For further details see the chapter on Dynamite, Stability Tests.

⁴³ *J. S. C. I.*, 41, 321, 324; *Z. Schiess- u. Sprengstoffw.* (1922), p. 158.

⁴⁴ *Mitt. Art.- u. Geniewesen* (1879), p. 349.

⁴⁵ *Mitt. Art.- u. Geniewesen* (1884), p. 202.

Stability on heating according to railroad regulations. The German Railroad regulations require for transportation of materials containing nitroglycerine, that the latter, subjected in whole cartridges continuously to a temperature of 75°C. for forty-eight hours, or in 10 gram samples in a closed weighing glass heated to the same temperature for the same time, shall not emit any acid vapors.

This test in a loosely covered weighing glass is also suited to determine the stability of nitroglycerine and all other nitric esters. Under these conditions absolutely stable nitroglycerine shows no visible decomposition products in forty-eight hours, such as yellow vapors, even though the vapors evolved color litmus paper red after the lapse of some hours. For a long time only traces of acid are given off, then the decomposition proceeds gradually, with development of yellow vapors of N_2O_4 , until finally, without any violent decomposition, there is complete decomposition and evolution of almost all the nitric acid in the form of nitric oxides, leaving behind an acid syrup composed of the products of the oxidation.

Decomposition of nitroglycerine at higher temperatures. A clear picture of the influence of the accumulation of nitric acid radicals in the molecule upon the chemical stability of the ester at higher temperatures is given by the comparative course of decomposition of three related nitric esters, according to tests made by the author (see table 4).

Nitroglycerine left behind 26.5 per cent of a thick, acid liquid, nitroglycol 29 per cent of a residue smelling strongly of acid and crystallizing on cooling, trimethylene glycol dinitrate remained unchanged for twenty-five days at 75°C., suffering only evaporation losses, and is therefore the most stable of the three esters, apparently because its molecule is less loaded up with nitric acid radicals than in the case of the nitroglycerine and nitroglycol molecules. The latter, in turn, is more stable than nitroglycerine, perhaps because its greater volatility removes the decomposition products so that they cannot act catalytically upon the decomposition reaction to as great an extent as with nitroglycerine.

The residues from both decompositions were easily soluble in water and reduced ammoniacal silver solutions. That from nitroglycerine contained traces of HNO_3 and no oxalic acid, while that from nitroglycol was completely free from HNO_3 and contained 25 per cent of oxalic acid.

Nitroglycerine can withstand even higher temperatures without a more profound decomposition for a rather long period, provided that the first traces of the products of decomposition are allowed to escape freely. The author heated 20 grams of nitroglycerine in an open weighing glass for six days without interruption at 100°C. After this period 60 per cent of it had evaporated. The residue had a slightly acid reaction but the unchanged nitrogen content of 18.40 per cent showed that it was still pure nitroglycerine.

Robertson⁴⁵ studied the decomposition of nitroglycerine at temperatures of 90 to 135°C., with elimination of the catalytic action of

TABLE 4
Comparative course of decomposition of three related nitric esters

LOSS OF WEIGHT	NITRO- GLYCERINE*	NITROGLYCOL*	TRIMETHYLENE GLYCOL DINITRATE*
	per cent	per cent	per cent
After 6 days.....	0.1	1.8	0.7
After 12 days.....	28.0†	4.2‡	1.8§
After 18 days.....	54.0‡	35.0†	2.7§
After 25 days.....	73.5‡	71.0‡	5.3§

* Ten grams each, heated to 75°C. in a loosely-covered dish.

† Decomposing.

‡ Decomposed.

§ Not acid.

¶ Acid.

Note: Nitroglycerine after three or four days had a strongly acid odor; after six days colorless vapors of HNO_3 were evolved on opening the glass and blowing over it; after ten days it emitted red vapors and was undergoing complete decomposition, while the nitroglycol was acid and giving off light-colored vapors.

the products of decomposition by drawing the latter off via a current of very pure carbon dioxide, and determined the decomposition products by a spectrograph and by reduction to nitrogen of the nitric oxide. He found that under these conditions the decomposition proceeded regularly and uniformly, as in an absolutely stable nitrocellulose, if the products of decomposition were constantly removed, but more rapidly than with nitrocellulose. All nitrogen was split

⁴⁵ Z. Schiess- u. Sprengstoffw. (1909), p. 301; Chem. News, 99, p. 289 (1909).

off as nitrogen dioxide. The decomposition is a function of the temperature, and from 95 to 125°C. it doubles for each 5°C.

Snelling and Storm⁴⁶ made extensive tests on the properties of nitroglycerine and its decomposition at even higher temperatures, showing that the course of the decomposition is strongly exothermic, and that nitroglycerine at the instant of final decomposition or detonation has an appreciably higher temperature than that of the heating bath. Several cubic centimeters of nitroglycerine were heated in a paraffin bath, and the temperature of both bath and sample followed by a thermometer or thermocouple. From 135°C. on the decomposition was clearly visible. The nitroglycerine became red from absorption of the products of decomposition. At 145°C. the decomposition and gas evolution became so rapid that the liquid apparently boiled. At 165°C. it boiled violently, and a distillate of dilute nitric acid and glycerine nitrates passed over, while the residue in this case consisted of glycerine and some mono- and dinitrates and other products of decomposition. At 180 to 185°C. the nitroglycerine became viscous, and at 215 to 218°C. there was a violent detonation.

PHYSIOLOGICAL PROPERTIES

Nitroglycerine is one of the organic poisons. Its action upon the human organism becomes evident in many individuals with even the smallest doses, and in such a case consists in migraine headaches enduring for hours, combined with a feeling of pressure in the front and back parts of the head. The severity of the effect varies. Those of a nervous temperament get a headache on merely entering rooms where nitroglycerine is being used and breathing the vapors, but if their stay there is for only a short time it rapidly disappears on getting out into the fresh air. The effect is much more severe if a small quantity only of nitroglycerine is absorbed by the unprotected skin and so gets into the blood current, as can occur very easily. The mucous membranes are most sensitive to this.

Alcohol raises the susceptibility to nitroglycerine. It also hinders acquiring an immunity to nitroglycerine, which with most persons occurs more or less rapidly when they are constantly exposed, and is of great importance for the work in most explosive plants. After one or more days most workmen become immune to the effects of nitro-

⁴⁶ *Z. Schiess- u. Sprengstoffw.* (1913), p. 1.

glycerine when breathed or absorbed by the skin, and no longer suffer from headaches. A cessation of exposure to nitroglycerine, even if for only a few days, makes a new immunization necessary. Only a few persons never become accustomed to nitroglycerine and have to give up the work. Those who are immune can be seen to mix nitroglycerine by hand with kieselguhr or nitrocotton, or rub guhr dynamite by hand through a screen, or smear their lower arms up to the elbow with the thin nitroglycerine-gelatine, which is then scraped off by the fingers. In general nothing is known regarding any harmful effect on the health, or any chronic effect of nitroglycerine upon such workmen in the dynamite plants.⁴⁷

Preventatives of the violent headaches which small quantities of nitroglycerine cause are those medicines which are of general use in cases of headaches, such as antipyrine, phenacetin, migraine pyramidon and aspirin. Black coffee is often recommended, but usually does not help. A walk in the fresh air brings relief if the effect is not too severe.

The workmen change their clothes before and after work, and also clean their faces, hands and finger nails well before eating, since penetration of nitroglycerine into the digestive canal is dangerous, more so than if it is only in contact with the skin.

If taken internally in considerable quantities nitroglycerine is a violent poison.

Schuchard⁴⁸ describes the symptoms on himself as follows: A drop swallowed caused headache, vertigo and dullness. More violent effects caused by larger quantities accidentally put into the throat were loss of consciousness changing to cold chills.

In recent times Weinberg⁴⁹ has published an extensive study of the physiological effects of nitroglycerine, considering as well the therapeutic use in the form of tablets containing 1 mg. of nitroglycerine, or a 1 per cent solution in alcohol called glonoin, largely used in England but less so in Germany, as regards the toxic effects, and

⁴⁷ See Hudson, *Med. Record*, January 20, 1917; and Ebright, *J. A. M. A.*, January 17, 1914.—TRANSLATOR.

⁴⁸ *Z. f. prakt. Heilkunde u. Medicinalwesen* (1866), H. 1; *Dingler*, vol. 180, p. 406 (1866). See also Bokorny, *Z. angew. Chem.* (1897), p. 337; and Law, *Trans. Med. Soc.* (1889).

⁴⁹ *Diss. Göttingen* (1910), and *Z. Schiess- u. Sprengstoffw.* (1911), p. 427.

giving abundant literature references. The different degrees of resistance of different individuals swallowing small quantities which he describes is very remarkable. Furthermore, the recorded fatal cases, usually caused by the accidental swallowing of large quantities, are set forth both as regards symptoms and course. According to Weinberg the greater part of the symptoms can be explained as nitrite effects, caused perhaps by the facts already proven by Schönbein, that all albuminates reduce nitrates to nitrites, a property ascribed to the living animal tissues and muscles. The symptoms in such severe cases consist mainly in violent cholic, vomiting, with final cyanosis and paralysis. Effective antidotes are not known, aside from immediate and thorough washing out of the stomach and intestines.

CHAPTER XIII

NITROGLYCERINE AS AN EXPLOSIVE

EASE OF DETONATION; SENSITIVENESS; ENERGY CONTENT; BRISANCE

Nitroglycerine, due to its peculiar chemical constitution, which renders possible decomposition into gaseous products with great development of heat, with an oxygen content more than sufficient for complete combustion of the carbon and hydrogen to carbon dioxide and water, is counted among the strongest of all known explosives.

The explosive decomposition of the molecule is as follows:



and can be started by heat, mechanical action such as a blow, shock or friction, and initial detonation.

DETONATION

1. *By heat.* Nitroglycerine cannot be exploded by mere contact with a flame because it is not particularly easy to ignite. A burning match immersed in it quickly goes out. A glowing platinum wire cools off, with some volatilization of the nitroglycerine. Contact with a burning splinter, also sparks from a burning black powder fuse, cause ignition. Small quantities, when once ignited, burn slowly with a slight crackling and a pale green flame. It is easily extinguished before it has all been consumed. On the other hand, if there is the possibility of any local overheating by radiation or conduction, as in burning in iron vessels, detonation can readily occur, also if large amounts catch fire, or if the rapid, exothermic reaction is induced by heat. By slow, careful heating small quantities can be evaporated without explosion, but never without decomposition. On the other hand, if small quantities are heated rapidly explosion always occurs at about 200°C. Nobel¹ gives the temperature of detonation on rapid heating as 180°C. According to the method generally used today, i.e., rapid heating of a small drop in a tube in a

¹ Nobel: *Dingler's* (1865), vol. 177, p. 167, and (1866), vol. 180, p. 243.

metal bath with a temperature rise of 20° per minute, the temperature of explosion is found to be 200 to 205°C. According to Snelling and Storm,² with larger quantities, such as several grams, the temperature of the nitroglycerine itself at the instant of explosion was 215 to 222°C. with the above bath temperature, because the rapid exothermic decomposition caused a spontaneous heating above the temperature of the bath at temperatures above 180°C. On allowing a drop of nitroglycerine to fall on an iron plate heated to successively higher temperatures the violence of the detonation decreases at the higher temperatures on account of the occurrence of a film of vapor between the source of the heat and the heated body, and at a red heat there is only a slight deflagration or rapid combustion and formation of the spheroidal condition.³ However, these statements are only true of small quantities. On heating larger quantities to 180°C. and above there is always an explosion.

2. *Detonation by mechanical effects.* Nitroglycerine is very sensitive to shock and blows. Its sensitiveness is not far different from that of percussion cap compositions. It is therefore designated as unsafe for transportation both in a pure condition and in solution, by the police regulations of September 14, 1905, and is excluded from trade.

It detonates readily by shock of iron on iron, or iron on hard rock, also porcelain on porcelain. When using softer metals like copper, brass or bronze the sensitiveness is much less, so that these latter are used as materials of construction for equipment and machines in which nitroglycerine is used. The shock of wood on wood is still less effective.

A drop of nitroglycerine on an anvil detonates when struck rather lightly by a hammer, especially if the oil is absorbed in filter paper. Usually the whole quantity does not explode, but only that portion directly under the hammer. However, the column of liquid explodes completely if the support on which it rests is rather small,⁴ such as a steel rod, or if a strip of tin foil is placed over it, so that in such a case the propagation of the wave of detonation seems to be favored.

² *Z. Schiess- u. Sprengstoffw.* (1913), p. 1.

³ Guttman, *Industrie der Explosivstoffe*, p. 442; Champion, *C. R.*, 73, 42 (1871); Kast, *Spreng- und Zündstoffe* (1921), p. 164 and the literature given there; Escales, *Nitroglycerin und Dynamit*, pp. 160-161.

⁴ Guttman, *Industrie der Explosivstoffe*, p. 441.

Various methods have come into use in the testing of the sensitiveness of explosives to shock and blows.⁵ That most widely used is the so-called falling weight test, which is best suited to compare the *relative* sensitiveness of different explosives, and for testing for permissibility under the regulations of the German railroad requirements.

The height of fall just necessary to cause detonation, and the size of the falling weight can be expressed as the work in kilogram-meters required to cause explosion. The quantity of the explosive and the construction of the apparatus are not without influence, and the exact comparison of different explosives is allowable only when using the same apparatus in the same manner.⁶ Different authors give very different values for the work required to detonate nitroglycerine, but in any case it is small, varying from 0.01 to 0.08 kg. according to recent data. According to Will, detonation occurs under a falling weight of 2 kg. at a height of 4 cm. According to Brunswig an explosion takes place under a 250 gram weight falling only 5 cm., and at 5 to 10 cm. with a 100 gram weight.

Heated nitroglycerine explodes more readily by shock.

Frozen nitroglycerine requires a stronger shock to detonate it than does the liquid, according to concordant data and as is to be expected theoretically. Even Nobel drew attention to this point,⁷ and Mowbray⁸ based his method of transporting nitroglycerine in a frozen state, used in America for a long time without accidents it is claimed, upon this fact. Beckerhinn⁹ found that three times as strong a blow was required to detonate frozen nitroglycerine as compared to the liquid state. Hess¹⁰ and Will¹¹ came to the same conclusions. The latter required a 10 cm. drop with a weight of 1 kg. to detonate liquid nitroglycerine at 15°C., and a 40 cm. drop for the frozen at -20°C. Cronquist¹² found a half-thawed mixture

⁵ Escales, *Nitroglycerin und Dynamit*, p. 157; Will: *Z. Schiess- u. Sprengstoffw.* (1906), p. 210.

⁶ See the work of Lenze and Mettagang on the use of the falling weight method, *Z. Schiess- u. Sprengstoffw.* (1906), pp. 287, 293.

⁷ *Wagner's Jahresbericht* (1869), p. 260.

⁸ *Dingler* (1869), p. 172.

⁹ *Wagner's Jahresbericht* (1876), p. 486.

¹⁰ *Mitt. Art.- und Geniewesen* (1876), p. 213.

¹¹ *Z. Berg.-, Hütten-, Sal-, Wes.* (1905), p. 26.

¹² *Oesterr. Berg.- u. Hüttenmänn. Z.* (1894), p. 221.

of liquid and solid nitroglycerine more sensitive than the liquid or the solid alone, and explained this by the friction of the very hard nitroglycerine crystals against each other.

A shot from a rifle explodes nitroglycerine, even from a distance of 150 meters.

Explosion can occur even from the rubbing in an unglazed porcelain mortar, as generally when rubbed between hard and rough surfaces.

3. *Detonation by initiating action.* The most reliable and the only method used in practice to detonate nitroglycerine and nitroglycerine explosives is the so-called initial detonation, i.e., the propagation of detonation from a blasting cap inserted into the nitroglycerine or the explosive to the latter. For a long time only mercury fulminate was known and used as the initiating explosive for filling blasting caps. Abel assumed as the cause of the detonation of large quantities of an explosive by a relatively small quantity of mercury fulminate a synchronism of the wave of explosion of the latter with the initiated explosive. This theory had to give way to that of Berthelot, who considered initiation as a mechanical percussion effect, especially after Wöhler discovered a series of other explosives which were also initiating agents and proved the relation existing between initiating effect and percussive effect.¹³

Sensitiveness to detonation

Although liquid nitroglycerine has a high sensitiveness to mechanical influences and can be readily exploded by blows and friction, it requires a relatively high initial impulse to cause propagation of the explosion and complete development of the energy it contains. As regards its sensitiveness to an initial impulse it does not assume first place among the related nitric esters of similar energy content. The ease of detonation without strong confinement by a weak impulse and with the maximum development of energy is the characteristic of high sensitiveness of any explosive to initiating impulse. If such a comparison of the three related and similar (as regards energy content) nitric esters nitroglycerine, nitroglycol and methyl nitrate is made, great differences are found. While with the weakest cap in

¹³ Wöhler and Matter, *Beitrag zur Wirkung der Initialzündung, Z. Schiess- u. Sprengstoffw.* (1907), p. 181.

use, a No. 1 containing 0.3 grams of fulminated-chlorate mixture,¹⁴ only 32 per cent of the energy of nitroglycerine capable of being released by the strongest commercial cap, a No. 8 containing 2 grams of the same mixture, is developed in the Trauzl block, this figure becomes 71 per cent with nitroglycol, and 84 per cent with methyl nitrate. The following summary of results obtained by the author makes it clear that in the case of nitroglycerine a comparatively higher initial impulse is required to develop the highest strength, provided the effect of pressure is not increased by a strong confinement.

TABLE 5

Results of placing 10 grams of each of the liquid esters in the cavity in the lead block, tamping with water, and firing

CAP USED	NET EXPANSION IN CUBIC CENTIMETERS WITH		
	Nitroglycerine	Nitroglycol	Methyl nitrate
No. 1 cap.....	190 cc. or 32 per cent	465 cc. or 71 per cent	520 cc. or 84 per cent
No. 3 cap.....	225 cc. or 38 per cent	—	—
No. 6 cap.....	460 cc. or 78 per cent	—	—
No. 8 cap.....	590 cc. or 100 per cent	650 cc. or 100 per cent	620 cc. or 100 per cent

The effect of the different caps themselves upon the lead block was not taken into consideration, because such differences were of no importance as compared to the great difference in expansion caused by the nitroglycerine.

Approximately equal amounts of energy were obtained with No. 8 caps from nitroglycerine and methyl nitrate, with methyl nitrate the No. 1 caps developed most of the possible energy, but hardly one-third in the case of nitroglycerine. The latter is therefore far less sensitive to detonation than the former. Nitroglycol approaches methyl nitrate in this respect.

These relations are apparently in accord with the viscosity of the liquids and the general observation that the explosive wave propa-

¹⁴ In the United States no blasting caps smaller than No. 6 are manufactured and there is a strong tendency toward increasingly large use of the No. 8 size.—TRANSLATOR.

gates with difficulty through rather immobile liquids. The very fluid esters nitroglycol and methyl nitrate detonate easier, although on the other hand, in interesting contrast to this relation, they are far less sensitive than nitroglycerine under the falling weight test.

If nitroglycerine be enclosed in a glass tube by a cork stopper, and placed in the lead block with sand tamping there is obtained:

With a No. 1 Cap.....	450 cc. net or 85 per cent
With a No. 8 Cap.....	520 cc. net or 100 per cent

The low velocity of detonation usually found, 1500 to 2000 meters per second, for nitroglycerine is also conditioned upon this relatively low sensitiveness.

That this behavior is only true of the liquid state is evident from the corresponding figures from guhr dynamite:

With a No. 1 Cap.....	285
With a No. 8 Cap.....	305

Therefore, when converted into a finely divided form nitroglycerine shows a high degree of increased sensitiveness. In this case the difference is only due to the cap. If 25 cc. is subtracted for a No. 8 cap, and 5 cc. for a No. 1 cap, 280 cc. is obtained in both cases, or with the No. 1 cap 100 per cent of the effect obtained with the No. 8 cap.

Propagation of detonation; velocity of detonation

Theoretically we understand by velocity of detonation that period of time in which the detonation of a unit of weight of the explosive is completed. In practice only the period of time can be measured which the wave of detonation requires to travel from one point on the material to another chosen point. Therefore in a practical sense the velocity of detonation is equal to the velocity of propagation of detonation.

The relatively low velocity of detonation which most investigators have determined by various methods is a peculiarity of liquid nitroglycerine. It is lower than that of most of the solid brisant explosives, and is confined to the liquid state. In the form of solid but appreciably less powerful explosives, such as guhr dynamite or gelatine dynamite, of which it is the main component, it shows a far higher velocity of detonation.

This velocity has been determined in lead, tin or iron pipes and found to be 1100 to 2000 meters per second, according to the internal diameter of the pipe.

Berthelot and Vieille¹⁵ found only 1100 meters per second in narrow lead or tin tubes 3 to 6 mm. internal diameter. Abel¹⁶ found 1525 m/s in a thin-walled lead pipe 30 mm. diameter. Mettegang¹⁷ found 2050 m/s in an iron pipe 30 mm. diameter.

In contrast to this, guhr dynamite in tubes 30 mm. diameter gives a velocity of detonation of 6000 meters per second, and gelatine dynamite 6500 meters.

However, under special conditions liquid nitroglycerine may also detonate with an extraordinarily high velocity, as recent results by Arthur Comey and Fletcher Holmes have shown.¹⁸ According to the method of Bichel and Mettegang in pipes 25 and 37.5 mm. diameter and with caps containing a 1.5 gram charge, they found irregular values ranging from the magnitude of the previous investigations, 1300 to 1500 m/s., up to 8000 to 8500 m/s.

By using a particularly efficient detonator, concerning the nature of which nothing is said, they then obtained regularly velocities between 6700 and 7500 m/s.

The authors, who found correspondingly great deviations in the crusher test, give no completely satisfactory explanation of the cause of these values, obtained by apparently similar methods of testing. Stettbacher¹⁹ mentions the possibility of the various velocities being due to the two isomers of nitroglycerine. This is apparently contradictory to the fact that Comey and Holmes presumably used the same material in a series of their tests. Apparently it may be that small differences in external physical influences, such as differences in the resistance of the iron pipes to rupture can be the cause of the low or high velocities.

Especially strong initial impulses, wide diameter and particularly good confinement may, according to general rules, favor the attainment of high velocities with nitroglycerine which usually detonates

¹⁵ *Mem. Poudre Salp.*, IV. 7 (1891).

¹⁶ *Phil. Transactions*, vol. 156, p. 269; vol. 157, p. 181.

¹⁷ *Internat. Kongressber.* (1903), II, p. 322.

¹⁸ *Z. Schiess- u. Sprengstoffw.* (1913), p. 306.

¹⁹ Stettbacher: *Schiess- und Sprengstoffe*, (1919), p. 125.

at a low velocity. According to Herlin,²⁰ frozen dynamite detonates without exception at the high velocity.

A similar behavior is shown by blasting gelatine containing 92 to 93 per cent nitroglycerine and 7 to 8 per cent collodion nitrocotton. It also has a low velocity of 1600 to 2000 m/s, and a high velocity of about 8000 m/s.

Here, however, a different physical condition of the material comes into consideration in that blasting gelatine containing air bubbles always assumes the high velocity, and transparent blasting gelatine almost always the low velocity of detonation.

Nitric esters of low viscosity and of similar energy content, such as methyl nitrate and nitroglycol, show higher velocities of detonation. The higher viscosity of a detonating liquid seems to hinder the propagation of detonation.

The products of explosion

Nitroglycerine contains somewhat more oxygen than is required to burn all the carbon and hydrogen on explosive decomposition of the molecule. On explosive decomposition according to the equation:²¹



1 molecule or 227 grams of nitroglycerine gives 132 grams CO_2 , 45 grams H_2O , 42 grams N_2 and 8 grams of O_2 , gaseous and vapor products. Therefore 1 kg. gives:

	grams	per cent*
CO_2	581.5	58.15
H_2O	198.2	19.82
N_2	185.0	18.50
O_2	35.3	3.53
	<u>1000.0</u>	<u>100.00</u>

*By weight

²⁰ Stettbacher: *Schiess- und Sprengstoffe* (1919), p. 125.

²¹ Kast, *Spreng- und Zundstoffe* (1921), p. 54 gives the following formula for the detonation of nitroglycerine: $32\text{C}_3\text{H}_5(\text{ONO}_2)_3 = 96\text{CO}_2 + 80\text{H}_2\text{O} + 6\text{NO} + 45\text{N}_2 + 5\text{O}_2$, wherein the formation of NO to a slight extent as an endothermic side reaction is assumed.

From the volume of the gases of explosion and the weight per liter we have:

	liters
CO_2	295.9
H_2O (vapor).....	245.8
N_2	147.5
O_2	24.7

that is, 713.9 liters of gas at 0° and 760 mm. pressure per 1 kg. of nitroglycerine. The composition of the gases of explosion in volume-per cent is therefore:

	per cent
CO_2	41.4
H_2O	34.6
N_2	20.6
O_2	3.4

The volume of the gases can also be very simply calculated by Avogadro's Law, according to which the molecules of all gases at equal temperatures and pressures occupy the same volume, so that the volume is calculated from the number of molecules contained. The molecular weight expressed in grams, of any gas at 0° and 760 mm. occupies a volume of 22.41 liters. Now since from 4 molecules of nitroglycerine (4 gram-molecules = 4×227 grams = 908 grams), according to the above equation 29 gaseous molecules are formed, it can be calculated that from 1 kg. of nitroglycerine the gas volume will be $29 \times 22.41/0.908 = 715.7$ liters at 0° and 760 mm. The deviation from the 713.9 liters above, obtained from the actual weights of a liter of the gases, is explained by the deviations from the gas law.

After condensation of the water 19 molecules of permanent gas remain, or $19 \times 22.41/0.908 = 469$ liters.

Almost the same figure is obtained by deducting 245.8 liters of water vapor from the above figure, or $713.9 - 245.8 =$ about 468 liters, consisting of 63.2 per cent CO_2 , 31.5 per cent N_2 and 5.3 per cent O_2 by volume. Sarrau and Vieille by the calorimetric bomb obtained 465 liters of permanent gas, reduced to 0° and 760 mm., or a figure coming very close to the calculated value.

A valuable property of nitroglycerine and guhr dynamite for underground use is that on proper detonation the products of explosion (fumes) are free from poisonous constituents, such as carbon

monoxide and nitrous gases. However, such gases occur when the nitroglycerine burns instead of detonating, in a so-called blown-out shot, as can occur with insufficient initiation from faulty caps. According to Sarrau and Vieille, burning nitroglycerine evolves gases of the following composition: 35.9 per cent CO, 12.8 per cent CO₂, 48.2 per cent NO, 1.3 per cent N₂, 0.2 per cent CH₄ and 1.6 per cent H₂.

Heat of explosion; temperature of explosion; pressure of explosion

The quantity of heat set free on explosion, which is the basis of the gas pressure and the work performed, is calculated from the sum of the heats of formation of the products of explosion, minus the heats of formation of the raw materials from the elements. The data in the literature vary somewhat with the constants used in the calculation.

The calculation based upon the heat of formation of carbon dioxide and water gives first the calories for constant pressure. However, this does not hold true in the case of explosives, because at the instant of explosion the volume of the products of explosion corresponds approximately to the volume of the explosive. The quantity of heat set free at constant volume is greater than that on decomposition in the free air and at constant pressure because the gases on dissipation into the air perform work, i.e., consume heat. Thus at constant volume there has been calculated for 1 kg. of nitroglycerine:

	Calories
According to Escales ²²	1470
According to Berthelot ²³	1478
According to Kast ²⁴	1455

These values are for water in the vapor state.

By inserting the somewhat higher heat of formation for liquid water there has been calculated for 1 kg. of nitroglycerine:

	Calories
According to Escales ²²	1589
According to Brunswig ²⁴	1580

²² *Nitroglycerin und Dynamit*, p. 169.

²³ *Spreng- und Zündstoffe*, p. 70.

²⁴ *Explosivstoffe* (1909), p. 6.

In the experimental determination in the explosion bomb the value for condensed water is determined. Sarrau and Vieille found 1600 Calories, or a value very close to the calculated.

Brunswig gives 415 Calories per kilogram as the heat of formation of nitroglycerine, and Kast gives 416 Calories. Escales gives 435.7 Calories.

The heat of explosion of nitroglycerine is calculated from the thermochemical data now generally assumed as follows:

I. Heat of formation:

	Calories per molecule
Of glycerine.....	161.7
Of water.....	68.3
Of nitric acid.....	45.8

$$161.7 + 3 \times 45.8 - 3 \times 68.3 = 94.2 \text{ Calories per molecule, or 415 Calories per kilogram}$$

II. Heat of explosion:

	Calories per molecule
Heat of formation of CO ₂	94.3
Heat of formation of H ₂ O (liquid).....	68.3
Heat of formation of H ₂ O (vapor).....	58.3



$$Q_p = 94.3 \times 12 + 68.3 \times 10 - 94.2 \times 4 = 1437.8 \text{ or } 359.45 \text{ Calories per molecule}$$

For the calculation at constant volume, or the work done by the explosion gases in displacing the air, with the consequent loss of heat, the following equation holds true:

$$Q_v = Q_p + 0.57n,$$

where n is the number of gaseous molecules (19 for 4 molecules of nitroglycerine). Therefore:

$$Q_v = 359.45 + 0.57 \times 4.75 = 362.16 \text{ Calories per molecule or 1595 Calories per kilogram with water liquid.}$$

(This value is to be compared with that determined experimentally, since in the measurement of the calories in the explosion bomb the water is in the liquid condition). By inserting the heat of formation of water vapor we have:

$$337.16 \text{ Calories per molecule, or 1485 Calories per kilogram}$$

The explosion temperature, or the quotient of the heat of explosion and the average specific heat of the products of explosion, cannot be determined experimentally, and only approximated by calculation. Brunswig gives this as 3470°C. for nitroglycerine. Recently Kast²⁵ has calculated the far higher value of 4250°C. Heise²⁶ gives 3158°, Gody 3153°, Auzenat 3469°, Wuich²⁷ 3035°, and the French Fire-damp Commission 3200°C. As a matter of fact, the highest temperatures attained on explosion are naturally lower than those given by the thermochemical calculation, because the ideal case assumes an exothermic reaction proceeding without loss of heat.

Explosion pressure

The maximum pressure which the gaseous products resulting from an explosive decomposition of an explosive exert on the surroundings can be calculated or measured. For calculation there is required a knowledge of the temperature of the explosion and the explosion volume, i.e., that volume which the gases of explosion would occupy at the temperature of the explosion, assuming the pressure remained constant. From the relation of the explosion volume to the volume of the original substance there is determined the gas pressure at the instant of explosion. The gas pressure is characteristic for each explosive.

Berthelot designates as "Specific Pressure" (f) that pressure exerted by a unit weight (1 kg.) of the explosive on explosion in a unit volume (1 liter or at a "Loading Density" of 1 at the explosion temperature (t)). Since according to the Mariotte Law the volume is inversely proportional to the pressure, we have:

$$f : p_0 = v_{0k} : v_{tk},$$

where p_0 is the atmospheric pressure (1.033 kg. per square centimeter), v_{tk} the volume at the temperature of explosion and 760 mm., and v_{0k} the volume at 0° and 760 mm., or

$$f = 1.033 \times v_{tk}$$

if 1 is assumed as a unit volume for v .

²⁵ *Spreng- und Zündstoffe*, p. 71.

²⁶ *Escales, Nitroglycerin und Dynamit*, p. 170.

²⁷ *Mitt. Art.- und Geniewesen* (1891), p. 67.

Since according to the Gay-Lussac Law

$$v_{tk} = v_0(273 + t) : 273,$$

we have

$$f = 1.033 \times v_0(273 + t) : 273$$

If in this equation is placed the 715.7 liters of explosion gases for nitroglycerine at 0° and 760 mm. and the explosion temperature according to Heise at 3158°, the specific pressure is found to be 9292 kg.

Co-volume. By co-volume is understood that space which the gas molecules themselves occupy, and which can no longer be diminished by any degree of compression. It amounts to about $\frac{1}{1000}$ of the volume occupied by the quantity of gas under consideration at 0° and 760 mm. The gases of explosion do not therefore have at their disposal the whole space in which the explosive is placed, but only a space diminished by the co-volume. The effect of the co-volume is to raise the gas pressure.

Density of loading. The actual maximum gas pressure is dependent upon the density of loading, Δ , or the quotient of the weight of the charge in grams and the explosion space in cc.

$$p = f \times \Delta$$

Measurement of the gas pressure. Direct measurement of the gas pressure is accomplished by the crusher gauge, the Nobel crusher gauge or the Bichel pressure gauge (German Patent 109187).

Energy content; work performed. Various ways have been proposed to express the relative value of the mechanical work performed (energy content) of an explosive. Berthelot²⁸ calls the product of the specific gas volume and heat of explosion the "characteristic product."

Moreover, the theoretical work performed by an explosive has often been expressed by multiplying the heat of explosion by 425, the mechanical equivalent of heat, and thus giving it in meter-kilograms.

Both expressions take no consideration of the velocity of detonation, a very important factor in the kind of explosive action, and one

²⁸ *Ann. chim. phys.*, 23, 223 (1871); and Berthelot, *Sur la force de la poudre et des matières explosives*, Paris, 1871.

TABLE 5
Comparison of other explosives with nitroglycerine

EXPLOSIVE	SPECIFIC VOLUME	EXPLOSION TEMPERATURE	EXPLOSION HEAT	CHARACTERISTIC PRODUCT	RELATIVE VALUE*
	liters	°C.	calories		
Blasting gelatine, 93 per cent nitroglycerine + 7 per cent nitrocotton	710	3,540	1,640	1,164,000	100
Nitroglycerine.....	712	3,470	1,580	1,125,000	97
Nitromannite.....	723	3,430	1,520	1,099,000	95
75 per cent guhr dynamite	628	3,160	1,290	810,000	70
40 per cent nitroglycerine dynamite.....	840	2,900	1,290	1,084,000	93
Nitrocotton, 13 per cent N	859	2,710	1,100	945,000	81
Gun cotton.....	830	2,400	900	747,000	64
Collodion nitrocotton, 12 per cent N.....	974	1,940	730	711,000	61
Ammonium nitrate dynamite, 90 per cent NH ₄ NO ₃ + 10 per cent nitronaphthalene.....	925	2,120	930	860,000	74
Picric acid.....	877	2,430	810	710,000	61
Black powder.....	285	2,770	685	195,000	17
Ammonium nitrate.....	937	2,120	630	590,000	50
Mercury fulminate.....	314	3,530	410	129,000	11

EXPLOSIVE	HEAT OF EXPLOSION	WORK DONE	RELATIVE VALUE*
	calories	meter-kg.	
Blasting gelatine, 93 per cent nitroglycerine + 7 per cent nitrocotton.....	1,640	700,000	100
Nitroglycerine.....	1,580	670,000	96
Nitromannite.....	1,520	645,000	92
75 per cent guhr dynamite	1,290	550,000	79
40 per cent nitroglycerine dynamite.....	1,290	550,000	79
Nitrocotton, 13 per cent N	1,100	465,000	66
Smokeless powder.....	900	380,000	54
Collodion nitrocotton, 12 per cent N.....	730	310,000	44
Ammonium nitrate dynamite.....	930	385,000	58
Picric acid.....	810	345,000	49
Black powder.....	685	290,000	41
Ammonium nitrate.....	630	265,000	38
Mercury fulminate.....	410	175,000	25

* Blasting gelatine = 100.

which is very considerably affected by the physical condition of the explosive, its aggregate state, its density, its crystal form, its granulation, as well as by external conditions of detonation such as the initiating impulse, confinement and tamping.

The values of other explosives are compared with those of nitroglycerine in table 6 by Brunswig.²³

Hess,²⁰ an officer of the engineers in Austria, in 1873 pointed out the defect in this method of expressing the maximum work done by an explosive, defined the conception of "brisance," and gave a method of determining it. He proposed brisance as the work done by a unit of weight of an explosive in a unit of time, and assumed a numerical value for this as the quotient of the Berthelot characteristic product and the time consumed by the explosion. This period of time was to be calculated from the experimentally determined velocity of explosion. However, this method of determining the work done by an explosive did not give complete agreement between calculation and experience.

This was even less the case with the Bichel³¹ formula, which deduced the kinetic energy of the products of explosion directly from the mechanical formula $\frac{mv^2}{2}$ and placed m equal to the mass of the explosive in kilograms, and v equal to the velocity of detonation. According to this formula the brisance must be proportional to the square of the velocity of detonation, indicating a unilateral tendency of this latter factor.

Kast³² then introduced the cubic density as a new factor in the evaluation of the maximum work done by an explosive. He advanced a formula which he himself called approximate, namely, $B = f \times d \times V$, where f = specific energy,³³ d = density, and V = velocity of detonation. In the measurement of brisance he found the so-called German crusher test very useful, provided the conditions of the test are properly chosen.³⁴ The test depends upon

²³ Brunswig, *Explosivstoffe* (1909), pp. 6 and 78.

²⁰ *Mitt. Art.-Geniewesen*, 4, 95, (1873).

³¹ *Glückauf*, 41, 465 (1905).

³² *Bewertung der Sprengstoffe nach ihrer maximalen Arbeitsleistung*, Z. angew. Chem. (1922), p. 72.

³³ Kast, *Spreng- und Zündstoffe*, p. 38.

³⁴ *Jahresber. d. Militärversuchsamt*, 9, 46 (1903); Z. Schiess- u. Sprengstoffw., 8, 88 (1913).

the fact that the detonating explosive imparts kinetic energy to a heavy steel piston, which is measured by the degree of compression of a small copper cylinder placed beneath it.

Work done in actual practice; explosive effect

Various more or less incomplete or one-sided empirical methods give a practical measure of the explosive effect of an explosive.

1. *The so-called Trauzl lead block test.* This test has been the most widely used test for obtaining a practical measure of the explosive strength of an explosive. It is a determination of the volume of the cavity produced by ten grams of the explosive to be tested when detonated in a given size of borehole in a cylindrical lead block.²⁶ The figure obtained is called the lead block expansion or lead block brisance. Naturally the volume of the original borehole is deducted from the final volume of the cavity. These volumes are determined by the amount of water required to fill the cavity. It is often customary to make a deduction also for the No. 8 blasting cap used to detonate the explosive. This amounts to 15 to 25 cc.

The method gives a reliable comparison of the practical effect only within a certain category of explosives, so that different ammonium nitrate explosives can be compared to one another very well, or various chlorate explosives, or various other dynamites. It should be particularly noted that the expansion with increasing energy is not an arithmetical but a geometrical progression, and therefore not strictly proportional. Ten grams of blasting gelatine apparently give more than twice the expansion of five grams.

For this reason it has often been proposed to evaluate explosives not from the expansion given by ten grams, but from a quantity which will always give the same average expansion of the lead block, amounting to 250 or 300 cc. From a strictly scientific basis this method would without doubt be logical and exact. However, this method has made little headway up to the present time in the practical testing of explosives at factories and testing stations, first perhaps on account of a certain conservatism, but mainly because it involves the expenditure of appreciably more time and money, because the weight in grams must first be obtained approximately from an average of a number of normal expansions, such an average weight then being

²⁶ Escales, *Nitroglycerin und Dynamit*, p. 176.

capable of giving the desired expansion. Furthermore, the deviations from the proportionality only become appreciable at very high expansions. With the lower and average expansions of most of the permissible and non-permissible explosives of commercial grades (200 to 400 cc.) this deviation does not render the result false to any appreciable extent. The results are considerably affected by the nature of the tamping. Fine, screened sand is commonly used (see Standards of the Fifth International Congress of Applied Chemistry).

This test can only be used with nitroglycerine if the liquid is detonated in a glass which fits air tight so to speak, in the borehole.

It is important to have the cork discs which seal off the liquid and which are perforated to receive the blasting cap, fit closely over the liquid without forming any air cushion, so as to give a maximum density of loading and allow the maximum quantity of sand tamping to be used.

The lead block expansion with nitroglycerine and the liquid nitric esters can be determined very simply by using water as tamping. This gives high values. Ten grams of the liquid is placed in the borehole with a cap having a waterproof fuse or an electric cap attached, and the hole filled to the rim with water, which is lighter than all the nitric esters.

Nitroglycerine is among those explosives standing at the top as regards lead block expansion, only being surpassed by methyl nitrate and nitroglycol.

Lead block expansion with water tamping

Tests made by the author are as follows, but somewhat lower expansions were obtained when using a glass container for nitroglycerine and the others, with sand tamping:

Nitroglycerine.....	cc. 590*
Nitroglycol.....	650
Methyl Nitrate.....	620

*With sand tamping 550 cc.

The fact that methyl nitrate, in spite of its 10.4 per cent oxygen deficiency and low energy content, shows a somewhat higher expansion than nitroglycerine, can be explained by its high velocity of detonation. Likewise the higher brisance of nitroglycol is not due merely to the more favorable oxygen balance, but just as much to

its higher velocity of detonation. Nitroglycol is balanced as regards oxygen content, while nitroglycerine contains a 3.5 per cent excess.

The lead block expansion furnishes a true picture of the total energy only for explosives of similar velocities of detonation. This latter property affects the results within certain limits. It is an essential factor of brisance, so that the expression "lead block brisance" is in a certain way justified for this test, although the lead block expansion mainly gives an expression of the specific energy of an explosive and is not influenced by density.

Non-brisant explosives such as black powder and blasting powder should not be compared with brisant explosives on the basis of the lead block expansion, since their expansion is comparatively low and does not express their practical performance.

Some types of explosives may be used to compare with the lead block expansion of nitroglycerine:

	cc.
Nitroglycerine.....	550
Nitromannite.....	560
Gum cotton, compressed, 13.2 per cent N.....	420
Blasting gelatine.....	580
Gelatine dynamite, 65 per cent.....	410
Guhr dynamite, 75 per cent nitroglycerine.....	325
Astralit, Donarit, Westfalit (ammonium nitrate dynamites).....	390
Koronit (potassium chlorate dynamite).....	290
Perchlorit, Permonit, Perkoronit (perchlorate dynamite).....	325
Detonit (Ammonium nitrate permissible).....	225
Nobelit (gelatine permissible).....	225
Tetranitromethylaniline.....	360
Picric acid.....	300
Trinitrotoluene.....	285
Dinitrobenzene.....	225
Mereury fulminate.....	150
Black powder.....	30

2. *Crusher test.* Often the Hess crusher test is used as a characteristic test of the effectiveness of an explosive. It shows the effect in the open air, without confinement or tamping, and is considerably affected by density, velocity of detonation and sensitiveness to initiation. Explosives which are very sensitive are the ones that exert the greatest effect without confinement. According to Hess two lead blocks 30 mm. high and 40 mm. diameter are placed one above the other, resting on an iron or steel plate. On top of the lead

blocks is placed a 4 mm. steel plate of the same diameter as the lead blocks, and the charge of explosive is placed on this steel plate. The charge is 50 to 100 grams. The deformation and compression of the upper lead block shows the effect of the explosive.

Often a single lead block 65 mm. high and 40 mm. diameter is used. Liquids must be placed in a sheet lead container of a suitable shape.

In this test nitroglycerine shows to an even greater extent than in the lead block test the effect of the relatively low velocity of detonation when in a liquid state and without confinement.

Nitroglycol and methyl nitrate, of higher velocity of detonation but of similar energy content, show considerable differences. The author found:

	mm.
Nitroglycerine.....	18.5
Nitroglycol.....	30.0
Methyl nitrate.....	24.5

Picric acid gives various compressions, depending upon the crystal form and density, ranging from 18 to 24 mm., in the latter case with severe deformation and tearing of the lead block.

If the nitric ester is converted into a solid form by absorbing it in kieselguhr, the above differences disappear, and 75 grams of nitroglycerine with 25 grams of kieselguhr gives considerably more compression than 100 grams of nitroglycerine alone. This comparison shows strikingly how little the lead block compression can be used as an expression of the total energy content. It gives rather merely a picture of the method of action, and in this case it is true to a remarkable degree, as has been said regarding the lead block expansion, that "As regards effectiveness, only explosives of the same class, and moreover with the same physical condition, can be compared."

	Lead block compression
Nitroglycerine 75 per cent } Kieselguhr 25 per cent }	23.2 mm.
Nitroglycol 75 per cent } Kieselguhr 25 per cent }	23.8 mm.
Methyl nitrate 75 per cent } Kieselguhr 25 per cent }	23.4 mm.

The crushing effect of pure nitroglycerine in a solid, powdery form has apparently not been tested. However, it is very probable that it would surpass the action of methyl nitrate and not differ appreciably from that of nitroglycol.

At times this test with liquid nitroglycerine has given an extraordinary effect, the block having been crushed much more than usual, or even torn to pieces. Here apparently the seldom observed high velocity of detonation of nitroglycerine has been released by some condition.³⁶

The other methods of testing the strength of explosives give with nitroglycerine less opportunity for characteristic comparisons which could be placed in the same class with the above.³⁷ For this reason those which have been included in older articles have been omitted.

³⁶ Stettbacher, *Die Schiess- und Sprengstoffe* (1919), p. 124.

³⁷ In the United States little work has been done in testing the strength of the different liquid explosives. For all solid explosives the manufacturers use the ballistic mortar, taking the recoil, as measured on a sliding scale as the strength, referred to pure trinitrotoluene or 40 per cent dynamite as the standard. The above lead block tests are not used.—TRANSLATOR.

PART II

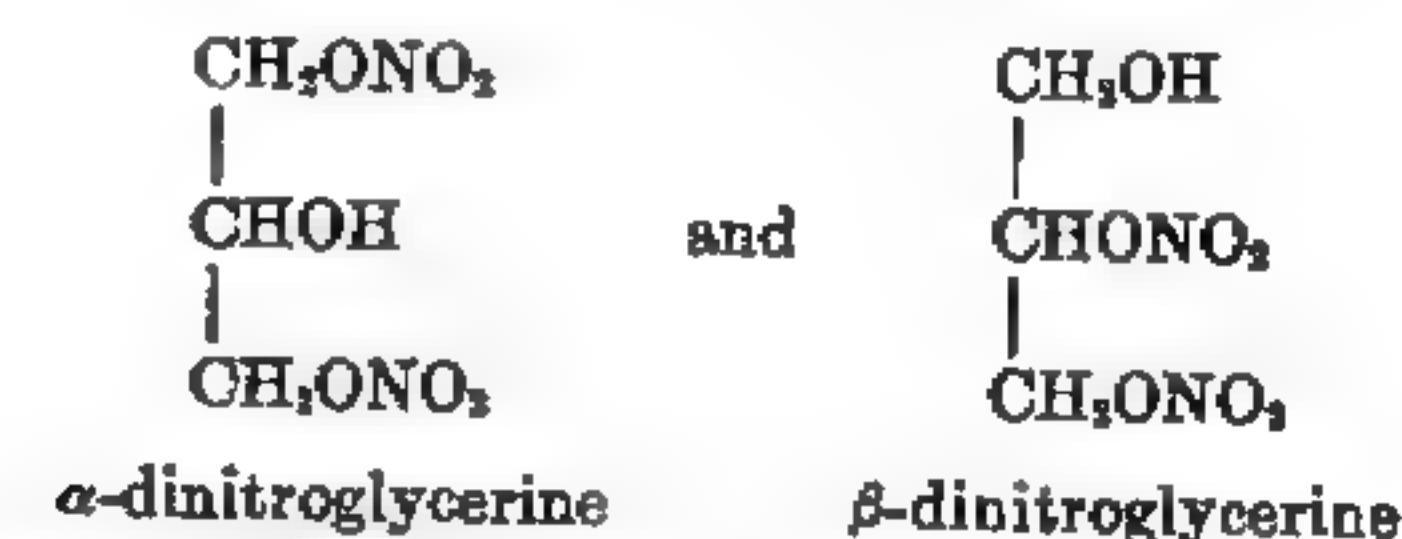
HOMOLOGOUS AND RELATED NITRIC ESTERS

CHAPTER XIV

THE LOWER GLYCERINE NITRATES

GLYCERINE DINITRATE (DINITROGLYCERINE)

Glycerine dinitrate, also called dinitroglycerine analogously to the nomenclature of nitroglycerine, exists in two structurally isomeric forms:



both of which have been made and identified. The commercial product is a mixture of the two isomers.

Historical. For a long time dinitroglycerine was absolutely unknown, although its preparation is not difficult. Even the literature contained hardly any data on its preparation and properties for a long time after nitroglycerine had been a commercial product. This is remarkable when it is remembered that, particularly in the older, imperfect processes of making nitroglycerine with weak acids, some dinitroglycerine was always produced as a by-product and could be recovered from the wash waters and spent acids by extraction. In any case, however, in former times the dynamite plants looked more toward the commercial and economic side of the manufacture of nitroglycerine, and the study of the scientific side of the reaction was neglected.

On the other hand, scientific institutions may have had a certain amount of disinclination to deal with the explosive nitric esters of glycerine. Thus it happened that this simple and thoroughly stable substance was as well as unknown up to the close of the century, and it remained for Dr. Anton Mikolajczak in 1903 to first describe the

methods of its manufacture and its properties, and to call attention to its commercial importance.¹

Dinitroglycerine was mentioned in 1865 by Liecke, but his statements were so inaccurate and of so little promise that it seems that he did not have pure dinitroglycerine.²

In German patent 58957, issued to Wohl, the solubility of mono- and dinitroglycerines in water was pointed out, and the suitability of the latter as a material to be added to nitroglycerine explosives to reduce the freezing point was mentioned. Wohl concluded that these glycerine nitrates are not very suitable for this purpose on account of their solubility in water and difficulty in preparing.

The commercial importance of dinitroglycerine depends upon the fact that it, in contrast to the readily freezing nitroglycerine, is very difficult to freeze. For Central European winter temperatures it can be considered as practically non-freezing, so that it was used for a certain time in the manufacture of non-freezing, plastic explosives. Mixed with nitroglycerine it lowers the freezing point and reduces the velocity of crystallization of the latter to such an extent that mixtures of 70 per cent nitroglycerine and 30 per cent dinitrate are very difficult to freeze, and mixtures of equal parts are non-freezing. Since dinitroglycerine itself is not much inferior to nitroglycerine in strength and brisance the properties of such mixtures do not differ very much from the latter, so that for a certain period such mixtures played an important part as the basis of "non-freezing dynamites" in the explosive art.

However very soon a competitor of dinitroglycerine for this purpose arose in dinitrochlorohydrine, the dinitrate of monochlorohydrine, which finally displaced it.

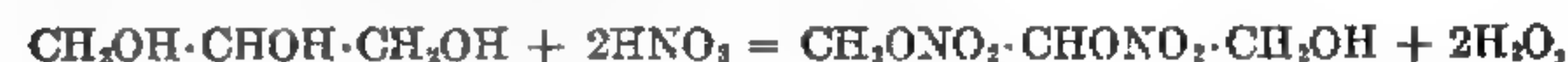
Dinitroglycerine had the disadvantage of a very appreciable solubility in water, making its manufacture inconvenient as compared to nitroglycerine and dinitrochlorohydrine, which are both insoluble in water. Moreover dinitrochlorohydrine has the advantage of a greater safety in handling, and can therefore be used as the basis of gelatinous, safe explosives, which is not the case with dinitroglycerine, which is not much less sensitive to mechanical action than nitroglycerine itself.

¹ *Glückauf*, 40, 629 (1904); *Bergbau*, 17, Nr. 45 (1904); same, 20, No. 35 (1907); Volpert, *Z. Schiess- u. Sprengstoffw.* (1906), p. 167; British patent 27706 (1904); French patent 341911 (1904).

² *Mitt. Hannov. Gewerbeverein* (1865), p. 214; *Dingler*, 179, p. 157, (1866).

For a number of years dinitroglycerine was made on a commercial scale in the Rummenohl plant of the Castropor Sicherheitssprengstoff-A.-G. later the Westdeutsche Sprengstoffwerke A.-G., but the manufacture was finally given up because it had no appreciable advantages over dinitrochlorohydrine, which could be produced more cheaply. Dinitroglycerine containing nitroglycerine was also used in the manufacture of gelatinous permissible explosives, but these also disappeared because just as high a degree of permissibility could be obtained with the cheaper nitroglycerine explosives, and no particular value was placed upon the non-freezing properties of this class of explosives because they were always stored under ground in frost-free mines. It appears that today the manufacture of dinitroglycerine can be considered merely as an episode in the art.

Method of preparation. Glycerine dinitrate is formed from glycerine and nitric acid according to the equation:



and theoretically 92 parts of glycerine and 126 parts of nitric acid give 182 parts of glycerine dinitrate and 36 parts of water. Therefore 100 parts of glycerine require only 137 parts of nitric acid monohydrate as against 205.4 parts for the trinitrate, giving theoretically 197.8 parts of the dinitrate as against 246.7 parts of the trinitrate.

Dinitroglycerine is formed if the esterification of glycerine by mixed acid or nitric acid is so conducted as to have either insufficient nitric acid present to completely convert the glycerine into the trinitrate, or if an insufficient dehydrating power of the acids fails to carry out the latter reaction.

Since this esterification proceeds by stages, embracing three possible steps, dinitroglycerine is never formed alone, but is always accompanied by the two other possible stages, namely the mononitrate and the trinitrate to a greater or lesser extent. There is no process known which gives the dinitrate in good yields without the simultaneous formation of some trinitrate. On the other hand, if the process is so conducted as to form the lowest possible yield of the trinitrate, the dinitrate is incompletely formed, and some mononitrate as well.

Methods of formation. 1. *Formation from nitric acid alone.* If glycerine is added to 3 to 5 times its quantity of highly concentrated nitric acid, a mixture of di- and trinitrate is formed after standing

for some time, which remains dissolved in the nitric acid. The less the nitric acid used the poorer the mixture in trinitrate. The more the nitric acid present the further is the esterification in the sense of trinitrate formation. The velocity of reaction is considerably less than in the esterification by mixed acid, and equilibrium is attained only after long standing, in some cases for several hours.

If a quantity of nitric acid equal to 3 to 4 times the weight of the glycerine is poured into the glycerine, so that at first the latter is in excess and never comes into contact with highly concentrated acid, mostly the dinitrate is formed, with a little mononitrate, while in the opposite case the glycerine first dissolves in the still highly concentrated acid, forming at first the trinitrate.

2. *Formation from mixed acid.* If glycerine is poured into a mixed acid high in water and low in nitric acid, there is formed nitroglycerine containing proportions of dinitroglycerine dependent upon the quantity and concentration conditions. The same thing occurs if the quantity of sulphuric acid present is insufficient to combine with the water up to the point of complete formation of the trinitrate.

3. *Formation by decomposition of nitroglycerine by sulphuric acid.* If nitroglycerine is dissolved in concentrated sulphuric acid, nitric acid is split off and dinitroglycerine formed, together with other decomposition products such as the mononitrate and glycerine sulphate. There may also be some unchanged nitroglycerine in solution, depending upon the degree of saturation of the sulphuric acid with nitroglycerine.³

For commercial manufacture only the Mikolajezak process is of importance. It was in practical use for a number of years by the Castrop-Sicherheitsprengstoff A.-G., later the Westdeutsche Sprengstoffwerke A.-G. at their Rummenohl plant at Hagen in Westfalia.⁴ It is based upon the solution of glycerine in nitric acid of a specific gravity 1.5, about 3 to 4 parts to 1 part of glycerine, maintaining this solution for several hours in order to complete the reaction (so called after-nitration), and neutralizing the solution diluted with ice and water with fine marble or calcite dust, forming a concentrated calcium nitrate solution of a higher specific gravity

³ Escales, *Nitroglycerin u. Dynamit*, p. 180, and Kast, *Spreng-u. Zündstoffe*, p. 168.

⁴ German patent 205752 to C. Pütz, and addition 225377 (1903). Also Heise, *Bergbau* (1907), No. 35.

than that of the dinitroglycerine, so that the oil which separates floats on the surface and can be withdrawn by a funnel in the usual way.

The oil is washed with a soda solution to remove the acid, and washed and dried by a special process.

The waste calcium nitrate liquor made from the unconsumed nitric acid is decomposed by a calculated quantity of ammonium sulphate into ammonium nitrate and calcium sulphate, the former being used in the manufacture of explosives, the latter as a fertilizer.

Preparation of pure dinitroglycerine. In order to obtain pure dinitroglycerine, free from nitroglycerine, the crude product is dissolved in a larger quantity (13 to 15 times) of water, separated from the undissolved nitroglycerine, and the aqueous solution extracted by ether. The dinitroglycerine obtained from the ether usually shows readily the Abel heat test reaction, which is due to the adhering oxidation products of the ether. The dinitroglycerine can also be obtained from the aqueous solution by distilling off the water under a vacuum. The product obtained shows no color in the Abel heat test even after one hour at 72°C. By repeated solution in water and extraction it can be freed from the last traces of nitroglycerine, and it then shows the theoretical nitrogen content of 15.38 per cent.

In thin layers over sulphuric acid, or by gentle heating at 40 to 50°C. the aqueous dinitroglycerine can be readily and completely dried.

German patent 210990 (1907)⁵ by Dr. Claessen describes a process for purifying dinitroglycerine containing 3 per cent water, consisting in mixing the latter with kieselguhr and crystallizing it in a freezing mixture, large quantities of the moist dinitroglycerine being placed in a freezing mixture and "seeded" with the frozen product. The crystalline hydrate can be recrystallized from water, alcohol or benzene. It melts at 26°C., and on heating goes over again into the anhydrous, oily dinitroglycerine (see next chapter).

Physical and chemical properties. Dinitroglycerine obtained by esterification of glycerine with nitric acid is a mixture of the two possible structural isomers (see introduction to this chapter). It has a specific gravity of 1.47 at 15°C. according to Will,⁶ 1.517 at

⁵ *Z. f. Schiess-u. Sprengstoffw.*, (1909), p. 333.

⁶ The specific gravity according to Will seems to be based on wet dinitroglycerine. When saturated with water it had a specific gravity of 1.47 according to the author's determinations.

20°C. according to the author's determinations, and 1.51 at 15°C. according to Blochmann,⁷ and is a colorless, odorless oil, more viscous than nitroglycerine, boiling at 146°C. under 15 mm. pressure with hardly any decomposition. The crystallizing point of the dry oil has not yet been determined. At temperatures of about -40°C. it solidifies to a glassy mass, which easily goes over into the liquid state again.

At ordinary temperatures and at a gentle heat it is only slightly volatile. The volatility when warm is about $1\frac{1}{2}$ to 2 times that of nitroglycerine. When the vapors are breathed, or the oil comes into contact with the skin it produces headaches like nitroglycerine. Like the latter it has a burning taste, and is apparently poisonous.

Solubility. As the di-ester of nitric acid it shows solubilities like those of nitroglycerine and is, for example, easily soluble in ether, acetone, alcohol and chloroform, somewhat less soluble than nitroglycerine in benzene, and insoluble in carbon tetrachloride and benzine.

On account of the hydroxyl group present it is considerably more soluble in water than nitroglycerine, although not very soluble. At room temperatures it dissolves in about $12\frac{1}{2}$ times its weight of water. At 15°C. 100 parts of water dissolve about 8 parts, at 50°C. about 10 parts. In dilute alkalies and acids it is very readily soluble. It dissolves in strong sulphuric acid, like nitroglycerine, splitting off HNO_3 and breaking down to mononitrate and glycerol sulphate.

Hygroscopicity. Dinitroglycerine is hygroscopic. In moist air it quickly attracts water up to 10 per cent, forming a hydrate of the formula $3(\text{C}_3\text{H}_5\text{N}_2\text{O}_7) + \text{H}_2\text{O}$ with a water content of 3.2 per cent. When heated to 40 to 50° or in a desiccator it loses the water readily.

Gelatinizing powers. Dinitroglycerine gelatinizes collodion nitro-cotton very rapidly, even at ordinary temperatures. However, the gelatine remains somewhat sticky, is less elastic and more easily deformed than that made from nitroglycerine. In moist air the gelatine becomes sticky and greasy from absorption of moisture, and loses its solidity. Moreover, water gradually dissolves the dinitroglycerine from it, leaving behind the nitrocellulose framework as a tough, stiff mass.

⁷ *Der Bergbau* (1905), Nr. 48; Escales, *Nitroglycerin u. Dynamit*, p. 186.

The isomeric forms of dinitroglycerine

The separation and determination of position of the two isomers of dinitroglycerine was due to Will and his associates Haanen and Stöhrer.⁸ They crystallized the mixture of moist product and kieselguhr by supercooling and "seeding" large quantities of the moist oil with frozen guhr mixtures. The larger part of the former crystallized in prisms, but a small part of the same chemical composition, separated and by further seeding, could not be crystallized.

K-Dinitroglycerine. The crystalline compound was called K-dinitroglycerine and showed itself to be the previously mentioned hydrate with one molecule of water to three of dinitroglycerine. It dissolves readily in water, alcohol and ether, difficultly in benzene, and from the latter it can be recrystallized very well. The crystals easily lose their water again on heating in the air or over sulphuric acid, and go over into the oily form, although they retain this water of crystallization on recrystallizing from water, alcohol, ether or even from benzene.

Benzoyl ester. On treating the K-dinitroglycerine with the calculated quantity of benzoyl chloride in aqueous solution with alkali, a dinitrobenzoyl glycerine having a melting point of 67°C. is obtained, insoluble in water, soluble in alcohol, ether and benzol, and readily recrystallized from alcohol with no water of crystallization.

p-I nitrobenzoyl ester. The action of p-nitrobenzoyl chloride in ether solution upon K-dinitroglycerine suspended in water, adding the calculated quantity of sodium hydroxide, forms the corresponding p-nitrobenzoyl ester, difficultly soluble in hot alcohol, and melting at 94°C.

P-dinitroglycerine. On drying the uncrystallized portion of the moist dinitroglycerine loses about 3 per cent water, like the crystalline variety. Both the aqueous and the dry product are shown to be chemically identical with K-dinitroglycerine, and agree with the latter in almost all their properties such as boiling points, solubilities, odor, taste, explosive character, etc. It is characterized by a different melting point (81°C.) and a ready solubility of the p-nitrobenzoyl ester in alcohol.

The different solubilities of the benzoyl and p-nitrobenzoyl ester permit determining the quantities in which both isomeric forms of dinitroglycerine form simultaneously under different conditions.

⁸ *Ber. d. d. Chem. Ges.*, 41, 1110 (1908), and *Z. Schiess-u. Sprengstoffw.* (1908), pp. 324 and 370.

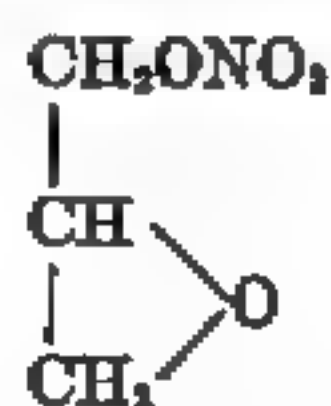
1. In the preparation by mixed acid (German patent 181385) there is a 70 to 75 per cent content of crystallizable dinitrate.

2. In the preparation by nitric acid alone (Mikolajczak Method) there is 60 to 65 per cent of the crystallizable dinitrate present.

The K-dinitrolycerine proves to be the symmetrical compound, $\text{CH}_2\text{ONO}_2 \cdot \text{CHOH} \cdot \text{CH}_2\text{ONO}_2$, and the F-dinitrolycerine the asymmetrical compound, $\text{CH}_2\text{ONO}_2 \cdot \text{CHONO}_2 \cdot \text{CH}_2\text{OH}$. The proof of the constitution is derived from the two isomeric glycerine mononitrates, and is therefore considered in the chapter on "Mononitrolycerine."

Chemical properties

Toward chemical reagents the two dinitrolycerines show the properties of nitric acid esters. They are easily decomposed by acids, splitting off nitric acid, and oxidizing. Sulphuric acid splits off HNO_3 and breaks them down to the mononitrate and glycerine.⁹ Saponification occurs with alkalis. Concentrated potassium or sodium hydroxide, as in the formation of epichlorohydrine from dichlorohydrine, causes one molecule of HNO_3 to split off and form KNO_3 , for example, and nitroglycide:



both dinitrolycerines forming the same nitroglycide, which with hot water goes over into the α -mononitrolycerine.

In other respects dinitrolycerine shows the properties of a weak acid. Even after complete removal of all traces of all mineral acids and in an absolutely stable condition it colors blue litmus paper a wine-red and dissolves readily in dilute alkalis. On the other hand it does not dissolve in a weak soda solution any more readily than in water and does not decompose carbonates, and is therefore a weaker acid than carbonic acid. The formation of characteristic salts of dinitrolycerine does not appear to have been accomplished as yet.

The hydroxyl group in dinitrolycerine is capable of further esterification. With concentrated nitric acid or mixed acid nitrolycerine

⁹ Analysis by nitrometer: N = 15.38 per cent.

is readily formed. With acetic anhydride acetyldinitrolycerine forms easily on heating, and in the same way benzoyl chloride forms benzoyldinitrolycerine.

Explosive character

Thanks to its composition, dinitrolycerine is an energetic explosive. The explosive decomposition is according to the following equation:



and can be induced by a sudden heating, mechanical effects or initiation, just as with nitrolycerine. The molecule lacks two atoms of oxygen for complete combustion to CO_2 and H_2O , or 100 parts of dinitrolycerine lack 17.6 parts of oxygen, so that the oxygen balance is -17.6 per cent.

The heat of explosion calculated according to the above equation is, with 116.7 Calories per molecule heat of formation, 1304.4 Calories per kilogram at constant volume and with water liquid, or 1201 Calories with water as vapor. The figure given by Blochmann¹⁰ of 942 Calories per kilogram as the heat of explosion is too low. Therefore dinitrolycerine is weaker than nitrolycerine, having only 81 per cent of the energy content of the latter. As regards sensitiveness to detonation there is no appreciable difference.

Behavior on heating; stability. On careful heating small amounts dinitrolycerine can be evaporated without explosion or deflagration. On platinum foil it deflagrates with a slight noise when heated rapidly. The same thing occurs with the hydrate after removal of the water. Heated in a glass tube it gives off red vapors above 150°C . Above 170°C . it undergoes violent decomposition with volatilization and slight deflagration. On heating larger quantities to this temperature there may be an explosion.

Stability. Stabilized dinitrolycerine exceeds nitrolycerine in stability and gives no discoloration to the paper even after one hour at 72°C .

Heat test at 75°C . It shows an appreciably higher stability than nitrolycerine on storing at higher temperatures, perhaps due to its chemical constitution or the smaller number of nitric acid radicals in the molecule. Ten grams in a loosely covered weighing bottle,

¹⁰ *Bergbau* (1905), No. 48; Escales, *Nitrolycerin u. Dynamit*, p. 186.

stored at 75°C., was still neutral after six days, and had only lost 0.1 per cent in weight from evaporation. A reaction occurred after fourteen days, forming some acid, with a loss of weight of 0.8 per cent. On further storage gradual decomposition took place.

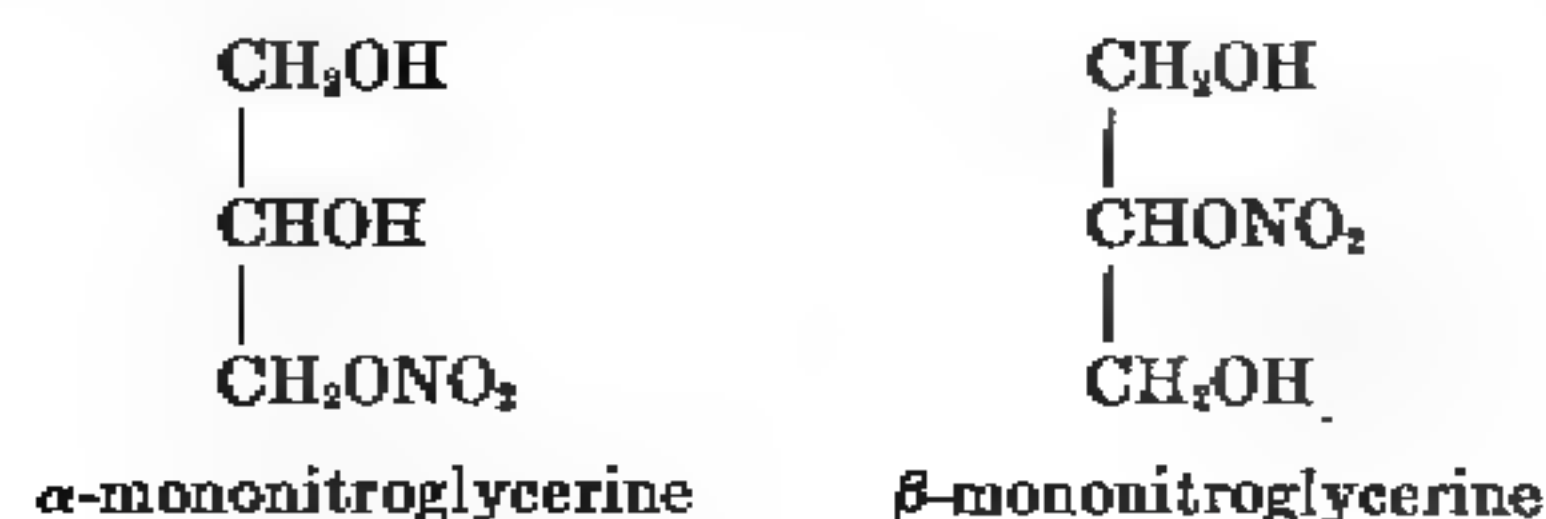
Sensitiveness to shock. The sensitiveness to shock is only slightly less than that of nitroglycerine.¹¹ Explosive mixtures containing dinitroglycerine behave correspondingly. The safety in handling dinitroglycerine and its preparation is therefore about the same as with nitroglycerine as regards mechanical effects.

Explosive effect. In the Trauzl block 10 grams of liquid dinitroglycerine with water tamping give about 500 cc. net expansion when detonated by a No. 8 cap, as against 600 cc. for nitroglycerine, and it is therefore 83.3 per cent the strength of the latter. The heats of explosion of the two, or 1201 Calories for dinitroglycerine versus 1485 Calories for nitroglycerine, are in the relation of 81:100. Therefore the lead block test furnishes a rather exact picture of the relations of the total energy contents of the two esters.

Crusher test. Dinitroglycerine also proves to be highly brisant in the crusher test. One hundred grams of dinitroglycerine in a lead container having walls 0.7 mm. thick and 40 mm. in diameter, with a wooden cover, loosely covered and detonated by a No. 8 cap, gave a 21 mm. compression to a lead block 65 mm. high and 40 mm. diameter. Under the same conditions nitroglycerine deformed the block considerably, with a compression of about 30 mm. The relation is therefore 70:100. The total energy content of dinitroglycerine is therefore less evident in this test, due to its lower velocity of detonation (see also dinitrochlorohydrine, explosive characteristics).

GLYCERINE MONONITRATE (MONONITROGLYCERINE)

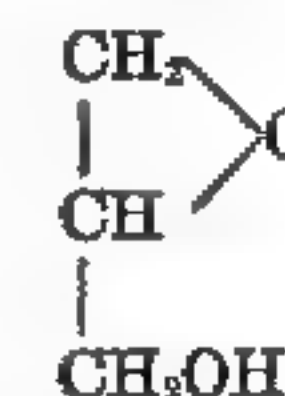
Glycerine mononitrate, the simple nitric ester of glycerine, exists in two structurally isomeric forms:



¹¹ See statements by Blochmann, *loc. cit.*

which have different melting points. They occur as by-products in the manufacture of dinitroglycerine, and although they can be detonated by a powerful initiating impulse, they are of no importance in the explosive art on account of their low energy content and high hygroscopicity, quite aside from their difficult and uneconomical manufacture.

They were first mentioned by Liecke in 1865 (see Dinitroglycerine, Historical), but his statements on the manufacture and properties appear unreliable. In 1879 Hanriot¹² obtained a mononitroglycerine by the action of dilute nitric acid upon glycide:



and described it as a compound readily soluble in water but difficultly soluble in ether, and which could not be exploded by shock.

Its preparation in a pure condition, its general characterization and proof of structure of the two isomers was due to Will and his associates¹³ (see Dinitrate). They obtained it by an ether extraction of the concentrated neutralization liquors from the preparation of dinitroglycerine.

Preparation. The author prepared it as follows: A mixture of 250 grams of concentrated nitric acid and 50 grams of concentrated sulphuric acid, very well cooled, was put into 100 grams of glycerine. Toward the end of the operation, a temperature of 5 to 10°C. being maintained, there was a great tendency toward oxidation, so that 300 parts of crushed ice was added at once, whereupon a small quantity of di- and trinitrate mixture separated, which was drawn off. It was then extracted several times with ether, and the ether solution neutralized.

The first extract yielded 26 grams of a mixture of 40 per cent di- and 60 per cent mononitrate. The second to eighth extracts inclusive gave 23 grams of pure mononitrate. The neutralized and evaporated solution gave 8 grams more of the mononitrate on extraction of the salt residue. Since 100 parts of glycerine theoretically give 149 parts of mononitrate the 47 grams obtained correspond to about 30 per cent of the theoretical yield.

Separation from the dinitrate: The separation of mono- and dinitrate is done

¹² *Ann. Chim. phys.* (5), 17, 118.

¹³ *Ber. d. d. Chem. Ges.*, 41, 1110 (1908), and *Z. Schiess- u. Sprengstoffw.* (1908), pp. 324 and 370.

by the different solubilities in water and ether. From a dilute solution of both nitrates in water ether easily removes the dinitrate. The mononitrate is then obtained by removal of the water in a vacuum, or by an intensive ether treatment of the concentrated solution.

Will crystallized the guhr mixture of the mononitrates by supercooling and seeded the first oily product. By working up the mother liquor from the mononitrate he then obtained a small quantity of the second isomer, from which the remainder of the other could be separated by crystallization. Also the second isomer, which was finally recognized as the β -form, was crystallized in admixture with guhr, and differentiated from the α -form by the melting point. An additional characterization was possible from the different melting points of the *p*-dinitrobenzoyl esters. From the total quantity of mononitrate only about 3 to 4 per cent of the β -nitrate could be isolated.

Preparation of pure α -mononitrate. The smoothest way of preparing pure mononitrate and obtaining almost exclusively the α -form, is from dinitroglycerine via nitroglycide. The latter is heated for a long time with water, and goes over into the α -mononitroglycerine by taking on one molecule of water, and by evaporation of the latter at a gentle heat or in a vacuum this can be isolated.

Properties. The mononitrate is usually obtained as a colorless oil, less viscous than glycerine but more so than dinitroglycerine. It has a very slight tendency to crystallize, and can be stored in the pure state for a long time without any crystallization. Even after melting the crystalline aggregate shows a pronounced tendency toward supercooling. The specific gravity of the liquid mononitrate is 1.417 at 15°C. according to the author, and 1.40 at the same temperature according to Will. The specific gravity of the crystalline α -form, on the other hand, is 1.53. The melting point of the α -form is 58 to 59°C., and of the β -form 54°C. according to Will. The boiling point of both isomers at 15 mm. is 155 to 160°C., also according to Will.

Mononitroglycerine has a rather bitter taste, and on the tongue or skin of sensitive persons causes headache. It is miscible in all proportions with water and alcohol, but in ether, on the other hand, it is relatively slowly and slightly soluble. It therefore approaches glycerine in its properties, and like the latter, is very hygroscopic. In contrast to glycerine, which is almost insoluble in nitroglycerine,

mononitroglycerine mixes with the latter. With collodion nitro-cotton it forms no complete gelatine.

Chemical properties. Mononitroglycerine acts like both a nitric ester and an alcohol. In the Lunge nitrometer it gives the calculated nitrogen content of 10.22 per cent. In contrast to K-dinitroglycerine it forms no hydrate, at least both of the known crystal forms are water-free.

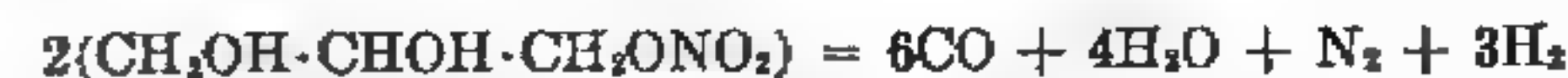
On moderate heating the material is absolutely stable, but when rapidly heated to 170°C. in a glass tube it breaks down and gives off a gas and turns yellow.

Reactions. The aqueous solution reacts neutral to litmus, so that mononitroglycerine is not an acid. With nitric acid mononitroglycerine forms dinitroglycerine and nitroglycerine, and with mixed acid readily forms nitroglycerine. Furthermore it easily forms mixed esters insoluble in water.

The diacetyl ester melts at 18 to 20°C., the dibenzoyl ester at 68 to 69°C., the *p*-dinitrobenzoyl ester at 139°C., all according to Will.

These figures refer to the derivative of α -mononitroglycerine. The *p*-dinitrobenzoyl ester of the β -compound melts at 52°C. The α -compound is moreover characterized by a double compound which it forms with calcium nitrate, $4C_3H_5(OH)_2ONO_2 + Ca(NO_3)_2$, which melts at 117°C. if recrystallized from alcohol. This compound is not formed by the β -variety.

Explosive character. As a possible explosive mononitroglycerine has a very unfavorable oxygen balance. The molecule lacks $4\frac{1}{2}$ atoms of oxygen for complete combustion, so that its oxygen deficiency is 52.5 per cent. Nevertheless an explosive decomposition is theoretically possible according to the following equation:



since this decomposition develops a quantity of heat amounting to 572 Calories per kilogram at constant volume with water liquid,¹⁴ the molecular heat of formation of mononitroglycerine being assumed as 139.4 Calories.

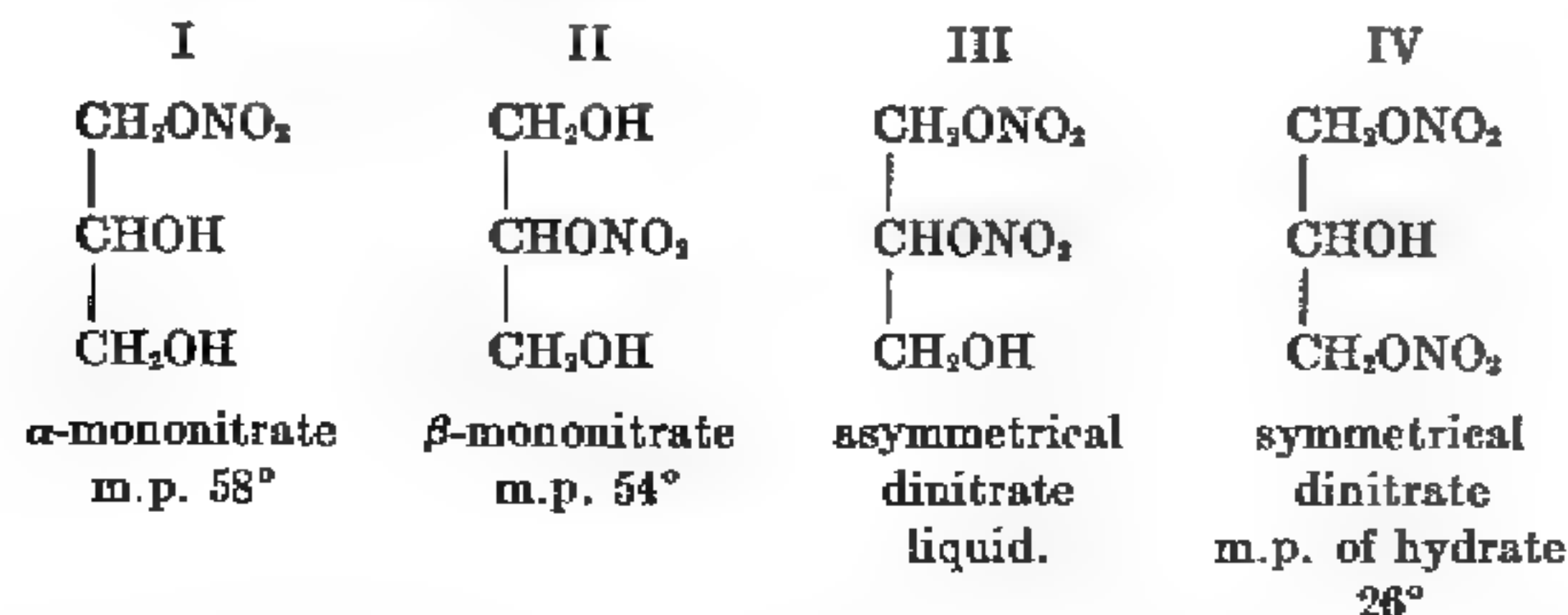
From the thermochemical point of view an explosion would therefore be expected, and in fact the product is clearly an explosive,

¹⁴ Or 434 Calories with water as vapor.

contrary to the data given by Will,¹⁵ since it can be readily exploded by an initiating impulse although under certain conditions it is rather insensitive.

It is very insensitive to blows and cannot be detonated in the falling weight test. Its detonation by a blasting cap depends greatly upon its physical condition. When in the form of an oil it cannot be detonated by a No. 8 cap in the lead block because of its viscous nature and relatively low development of heat. A weak and partial detonation occurs if it is absorbed in kieselguhr and so changed to a powder. In this condition 10 grams gives 75 cc. net expansion with development of vapors of acrolein. The crystalline product, however, detonates easily in the lead block, with the very substantial net expansion of 245 cc. Here the relation of energy content and strength developed in the lead block between nitroglycerine and mononitroglycerine approximately correspond. With 572 Calories mononitroglycerine has about 36 per cent of the energy content of nitroglycerine, which has 1595 Calories, and gives a net expansion of 550 cc. with sand tamping, as compared to the 245 cc. for mononitroglycerine, or 44.5 per cent the strength of nitroglycerine, which is a fair agreement if the inaccuracy of the lead block figures in general is taken into consideration, as well as the fact that the mononitroglycerine was detonated as a crystal powder, the nitroglycerine as a liquid.

*Proof of the constitution and determination of position of the isomeric glycerine mononitrates and dinitrates:*¹⁶

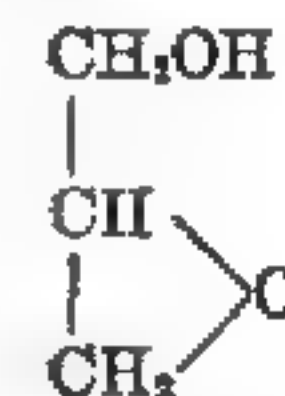


The fact that the mononitrate melting at 58°C. is formed from the nitroglycide by boiling with water shows that it contains the nitric

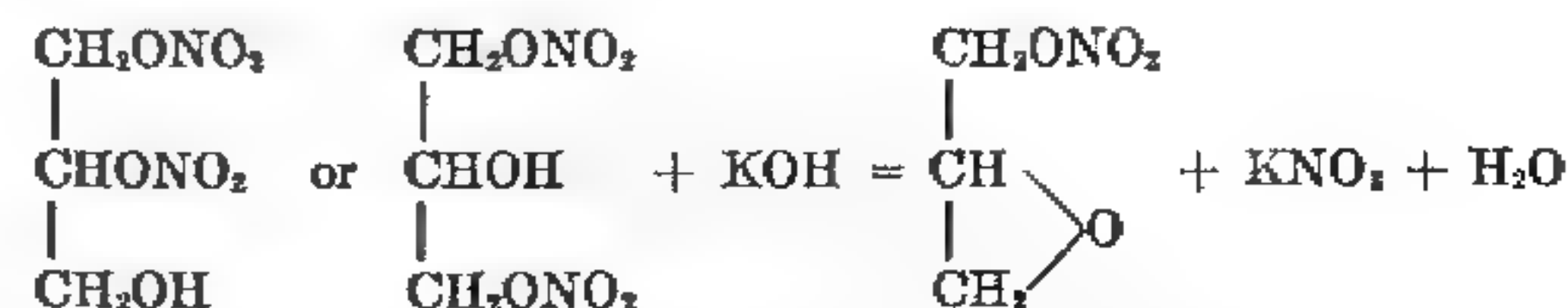
acid group in the α-position. The α-substituted mononitrate should give two dinitrates on further treatment with nitric acid, but the β-substituted variety only one, namely the asymmetrical dinitrate. As a matter of fact, Will obtained both dinitrates from the mononitrate melting at 58°, and from that melting at 54° only one, which formed no crystalline hydrate. Therefore the mononitrate melting at 58°C. corresponds to the α-compound of Formula I, and that melting at 54°C. to the β-compound of Formula II. The dinitrate formed only from the α-mononitrate and not from the β-mononitrate must be the symmetrical one. It is that forming a crystal hydrate melting at 26°C., corresponding to Formula IV. The dinitrate obtained from both mononitrates can only be the asymmetrical. This is the liquid which must accordingly correspond to Formula II.

NITROGLYCIDE, A DECOMPOSITION PRODUCT OF DINITROGLYCERINE

Nitroglycide, the nitric ester of glycide,



the internal anhydride of glycerine, cannot be obtained by direct esterification of glycide because of the easy break-down of the oxygen bond, since it is immediately transformed by acids. It is formed from dinitroglycerine, even from both isomers, by treatment with concentrated alkalis, splitting off a molecule of HNO₃ according to the following equation:



Although it has found no application up to the present time in explosive technique, it is of interest on account of its chemical properties and its high explosive strength and sensitiveness in comparison to mononitroglycerine, closely related to it as regards synthesis and oxygen balance.

¹⁵ Ber., loc. cit.

¹⁶ Will, loc. cit.

Preparation. Nitroglycide was first made by the author in 1907 as follows: One hundred grams of dinitroglycerine free from trinitrate was shaken at room temperatures with 225 grams of 30 per cent sodium hydroxide. At first a clear solution was formed, and then after about one minute the liquid became milky and a very mobile oil settled out, which was washed several times with water and dried in a desiccator. The reaction was accompanied by a very slight evolution of heat, the temperature rising only about 1 to 2°C. The yield was 62 grams or 95 per cent, the theoretical being 65.4 grams.

Analysis. Since the oil exploded at once in contact with sulphuric acid it was first suspended in dilute sulphuric acid for the Lunge nitrometer determination, and added drop by drop to well cooled concentrated sulphuric acid to avoid development of heat, until it dissolved completely. The solution was then washed quantitatively into the nitrometer by means of concentrated sulphuric acid. The nitrogen content was found to be 11.75 per cent, the calculated being 11.87 per cent.

Physical properties. Nitroglycide is a water-white, very mobile liquid with a slight, pleasant, aromatic odor and a specific gravity of 1.332 at 20°C. It does not freeze at -20°C., boils at 174°C. to 175°C. at ordinary pressures, but not without some decomposition such as evolution of nitrous vapors, or at 94°C. under a pressure of about 20 mm. It is very volatile at ordinary temperatures. The loss in weight of a small quantity exposed at room temperatures in a shallow dish after thirty hours was 10 per cent, at 40°C. for four hours 35 per cent, and at 100°C. for two hours there was complete evaporation. The oil is not hygroscopic, but dissolves in water, about 5 grams per 100 cc. at 20°C. If the solution is not warmed ether will extract the nitroglycide unchanged.

Solubility. The oil is miscible in all proportions with alcohol, ether, acetone, ethyl acetate and nitroglycerine.

Gelatinizing properties. The oil gelatinizes collodion nitrocotton and even gun cotton immediately even at room temperatures.

Chemical properties. 1. With concentrated sulphuric acid the reaction is so violent and accompanied by so great evolution of heat that even with very small quantities there is an almost instantaneous explosive deflagration, accompanied by a flame and charring of the residue. With dilute sulphuric acid there is at first no reaction. If concentrated sulphuric acid is added gradually solution occurs with decomposition and splitting off HNO_3 .

2. The oil dissolves in concentrated nitric acid with a great development of heat and formation of dinitroglycerine and nitroglycerine. On dilution with water the latter precipitates.

3. In concentrated hydrochloric acid the oil dissolves with considerable evolution of heat and addition of one molecule of HCl . On dilution with water an oily monochlorohydrine mononitrate partly precipitates.

4. The oil is saponified to glycerine by boiling alkalies.

5. Halogens act very slowly, with formation of substitution products.

6. Ammoniacal silver nitrate solutions are slowly reduced on gentle heating. Glycide reduces these even in the cold.

7. Boiling water converts nitroglycide into α -mononitroglycerine, with addition of one molecule of water.

Explosive character. In spite of its unfavorable oxygen balance, 100 parts requiring 60.5 parts of oxygen for complete combustion, nitroglycide is a highly brisant and very sensitive explosive, and is an interesting contrast in this respect to the closely related mononitroglycerine, whose anhydride it is.

While the latter is very insensitive and difficult to start off and not capable of being exploded when in a liquid condition by either shock or blasting cap, nitroglycide explodes under the falling weight test at very low drops, 0.2 kg.-meters, or with a 10 to 20 cm. drop of a 2 kg. weight, and when in a liquid condition it explodes easily with a blasting cap and develops considerable brisance.

In the Trauzl lead block

10 grams liquid nitroglycide with water tamping and No. 8 cap gave 430 cc. net

10 grams liquid nitroglycide with water tamping and No. 1 cap gave 370 cc. net

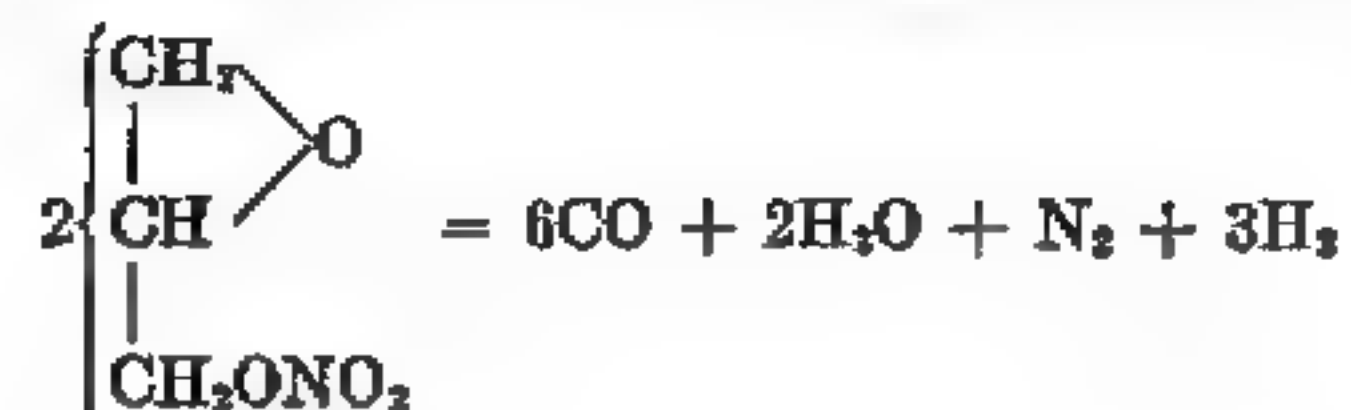
10 grams nitroglycide absorbed in kieselguhr, sand tamping gave 310 cc. net

10 grams nitroglycide gelatinized with 5 per cent collodion nitrocotton, with sand tamping gave 395 cc. net

On rapid heating in a test tube the oil exploded with a sharp report at 195 to 200°C. In contact with a flame at ordinary temperatures it ignites easily and burns vigorously with hissing.

The easy explosive decomposition of nitroglycide is particularly characterized by the fact that it explodes even with the weakest blasting cap, a No. 1, giving 86 per cent of the explosive effect obtained with a No. 8 cap. If the values of expansion produced by the caps in question with water tamping, namely 30 cc. for the No. 8 and 7 cc. for the No. 1, are deducted, the relation becomes 91:100. With nitroglycerine this relation is 32:100. Therefore nitroglycide detonates more easily than liquid nitroglycerine.

This high sensitiveness, particularly in contrast to the closely related but inert mononitroglycerine, depends mainly upon the easy propagation of the wave of detonation by a liquid of low viscosity. Also perhaps in this case the nature of the chemical structure of the molecules, i.e., the easy mobility of the anhydride oxygen atom, plays a special part, while the thermo-chemical difference is not sufficient to explain the fundamental contrast between the sensitiveness to detonation of the liquid mononitroglycerine and the liquid nitroglycide. The latter decomposes according to the equation:



with development of 824 Calories per kilogram at constant volume and water liquid, or 745 Calories per kilogram with water gaseous, the molecular heat of formation being taken as 51.4 Calories. Mononitroglycerine, with 572 Calories, has 69.5 per cent of the energy content of nitroglycide, and as a crystal powder and under sand tamping a lead block expansion of 245 cc., or only about 62 per cent the strength of nitroglycide, so that a higher velocity of detonation must be assumed for the latter. Similar relations hold between nitroglycide and the powerful nitroglycerine. The energy contents, 1595 and 824 Calories, are as 100:52. On the other hand, nitroglycide with 430 cc. expansion has 72 per cent the explosive effect of nitroglycerine, with 600 cc. expansion. It is therefore relatively more brisant than nitroglycerine.

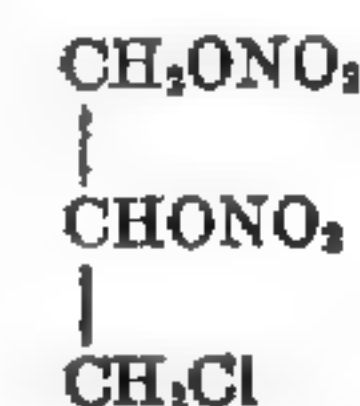
CHAPTER XV

MIXED EXPLOSIVE GLYCERINE ESTERS

NITRATES OF THE CHLOROHYDRINES

Monochlorohydrine dinitrate (dinitrochlorohydrine)

Of all the nitric esters related to or homologous with nitroglycerine, up to the present time in Germany mainly the dinitrate of monochlorohydrine, the so-called dinitrochlorohydrine



has become of permanent commercial importance. Among the explosive nitric esters proposed as additions to nitroglycerine to reduce the freezing point of the latter in the first decade of the century, namely dinitroglycerine, tetranitrodiglycerine, nitroglycol, acetyldinitroglycerine, etc., up to the present time dinitrochlorohydrine has been preferred in Germany because of its convenience and smooth, safe manufacture.¹ In addition to this should be mentioned its favorable properties such as insolubility in water, explosive strength and moderate volatility.

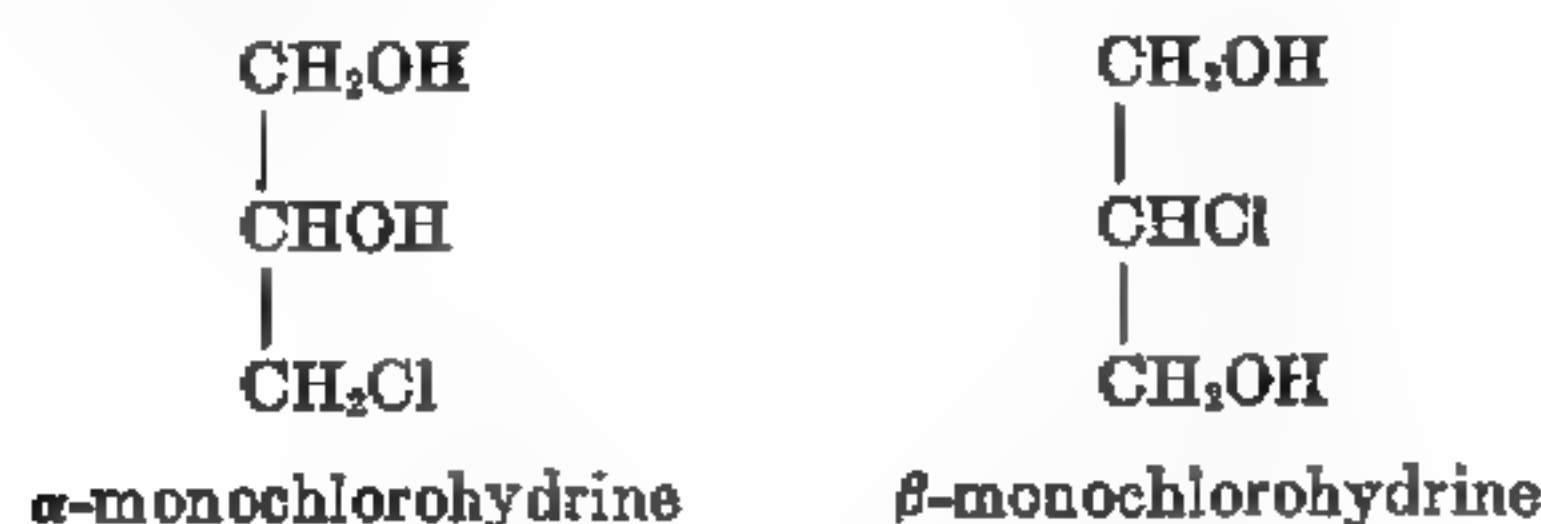
Its relatively low sensitiveness to shock and heat as compared to nitroglycerine is a point in its favor, so that it can form the basis of gelatinous explosives similar to dynamite, which surpass the gelatine dynamites in safety in handling to a considerable extent, and therefore enjoy in Germany a preference in requirements for railroad transportation.

Dinitrochlorohydrine was also used for a long time in the manufacture of safety and permissible gelatinous explosives.

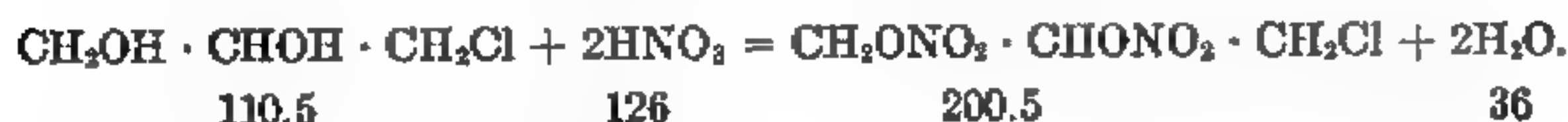
¹ In the United States dinitrochlorohydrine was used for a short time by the former Aetna Explosives Company, but for the last decade or so the greater part of the explosives have been made with diglycerine tetranitrate.—
TRANSLATOR.

It was first prepared by Henry,² and first mentioned as an explosive component by Volney in 1881.³ However, at that period there seems to have been no appreciable introduction of the product into explosives. In 1904 it was patented and introduced as a means of manufacture of non-freezing, plastic explosives by the Dynamit A.-G. vormals Alfred Nobel & Co.⁴ From this time on it found commercial use, not in a pure condition but in admixture with nitroglycerine, made by nitrating corresponding mixtures of monochlorohydrine and glycerine.⁵

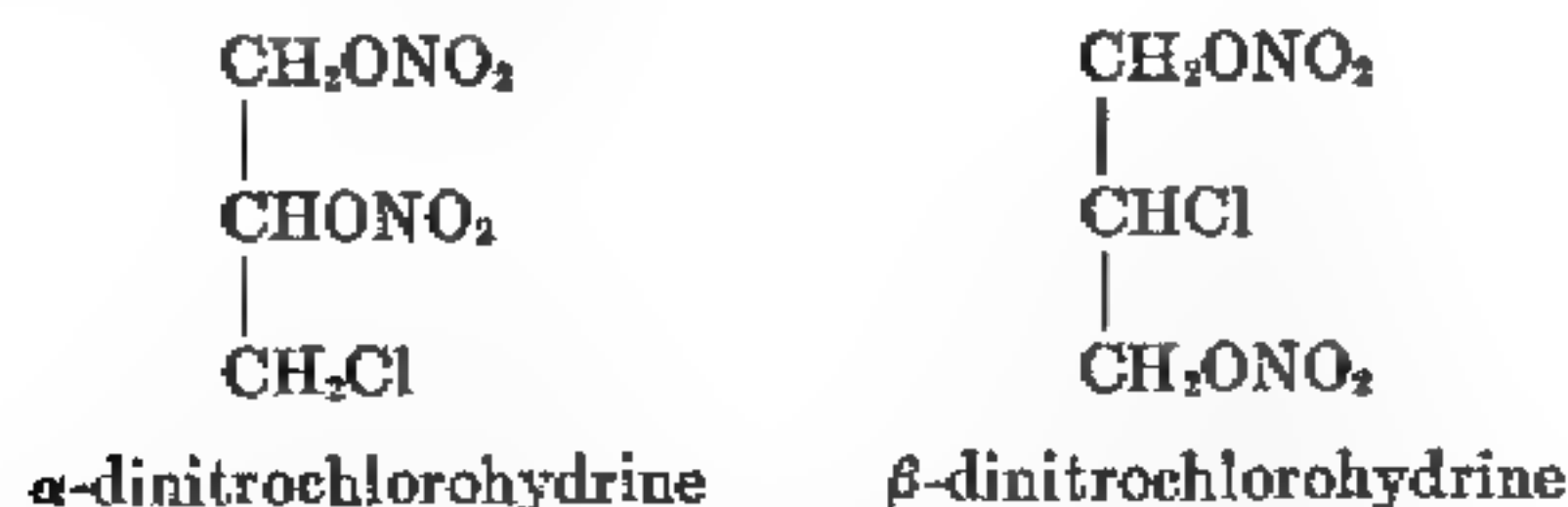
Method of formation. Dinitrochlorohydrine is formed in two isomeric modifications; from



by esterification with nitric acid according to the equation:



Of the two structural isomers:



the commercial product contains mainly the former.

Therefore 100 parts of monochlorohydrine require for esterification 114 parts of HNO₃ and theoretically give 181.45 parts of dinitrochlorohydrine and 32.6 parts of H₂O. To form 100 parts of

² C.R., 70, p. 860 (1870); Ber., 3, p. 347 (1870); Liebig's Ann., 155, p. 165 (1870).

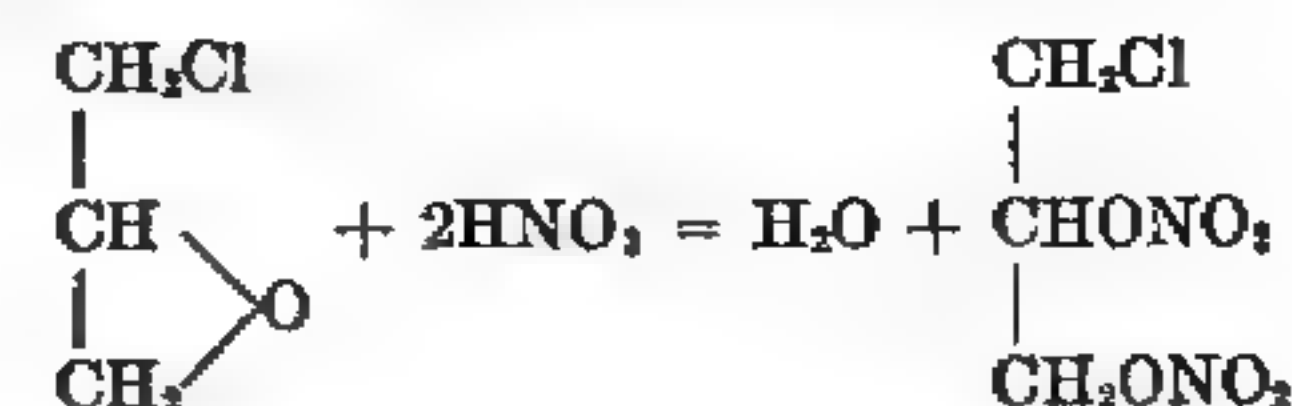
³ United States patent 249490 (1881); Z. Schiess- u. Sprengstoffw. (1909), pp. 405 and 456, and (1910) p. 361.

⁴ German patent 183400; Belgian patent 185513.

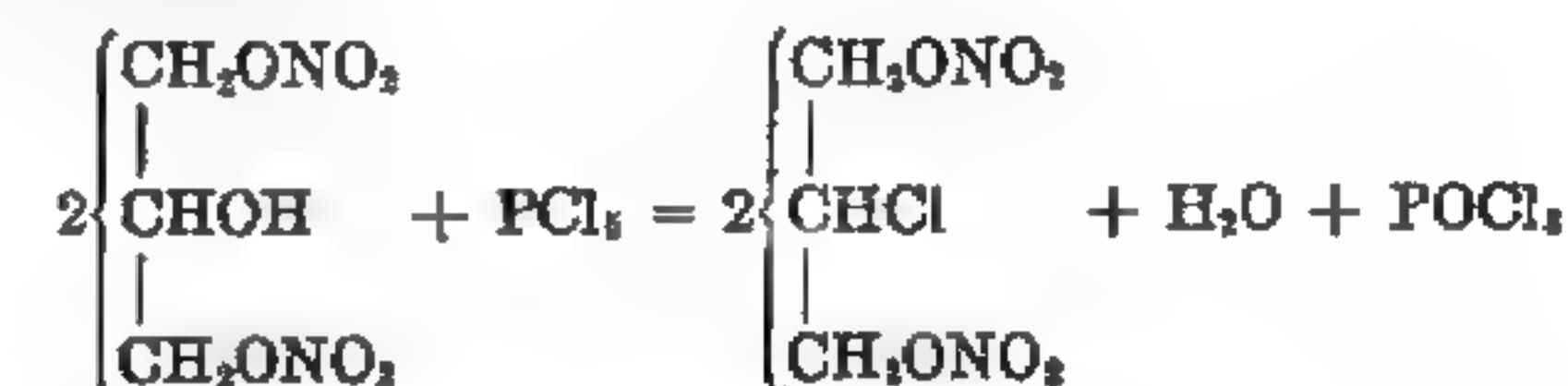
⁵ Z. Schiess- u. Sprengstoffw. (1906), p. 229; Bergbau, 40, No. 43 (1907).

dinitrochlorohydrine therefore requires 55.1 parts of chlorohydrine and 62.8 parts of HNO₃.

The α-dinitrochlorohydrine (asymmetrical) is formed by the action of concentrated nitric acid on epichlorohydrine:



while the β-nitrochlorohydrine (symmetrical) is prepared by the action of phosphorus pentachloride on a chloroform solution of symmetrical K-dinitroglycerine:



Method of preparation and manufacture. It is made by gradually adding monochlorohydrine, with good cooling and agitation, to a mixed acid, just as in the manufacture of nitroglycerine, in the same apparatus, and usually with the same mixed acids, but naturally with a smaller quantity of mixed acid per unit of weight of monochlorohydrine than with glycerine, corresponding to the lower consumption of nitric acid and the smaller quantity of water to be fixed.

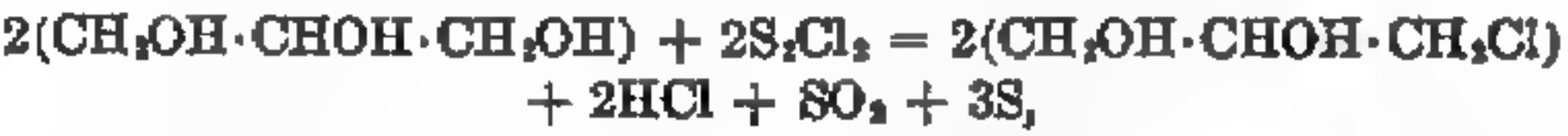
Raw materials. (a) *Mixed acid.* Usually the same mixed acid is used as for the manufacture of nitroglycerine.

(b) *Monochlorohydrine.* Before it obtained importance as a raw material for dinitrochlorohydrine, monochlorohydrine was made to only a limited extent, and the process was therefore practically unknown as far as profitable manufacture was concerned. This was developed as its importance in the art of explosive manufacture became known. Monochlorohydrine can be made either by the chlorination of glycerine at high temperatures and under pressure in autoclaves with concentrated hydrochloric acid, or by chlorination at moderate temperatures by means of sulphur chloride. The product obtained by the first process is always more or less contaminated by dichlorohydrine, at least if complete chlorination of the glycerine is obtained, while the second process can be so conducted as to give almost wholly the monochlorohydrine.

According to German patent 180668, issued to the Deutsche Sprengstoff-A.-G.¹ the monochlorohydrine is obtained by heating glycerine with aqueous hydrochloric acid of specific gravity 1.185, in autoclaves for fifteen hours at 120°C. After driving off the water, the excess of hydrochloric acid and some of the dichlorohydrine formed, there remains a mixture of about 75 per cent monochlorohydrine and 25 per cent unchanged glycerine, from which the monochlorohydrine can be recovered by fractional distillation in a vacuum. In actual practice the mixture is nitrated direct, giving a mixture of dinitrochlorohydrine and nitroglycerine.

Example. 100 kg. of dynamite glycerine was mixed at ordinary temperatures with 150 kg. of aqueous hydrochloric acid of a specific gravity 1.18-1.19, and heated for fifteen hours in an autoclave at 120°C., or at a positive pressure of 1 atmosphere. The chlorinated material was subjected to fractionation in a vacuum distillation at 12 to 15 mm. pressure, the water vapor and unconsumed hydrochloric acid coming over first. Between 130 to 150°C. the monochlorohydrine passed over, and between 165 to 180°C. the unconverted glycerine. When used for making nitroglycerine and its mixtures the latter distillation, or the separation of the monochlorohydrine from the glycerine, is usually omitted.

According to French patent 370224, issued to the Deutsche Sprengstoff-A.-G., the monochlorohydrine is obtained almost exclusively in good yields if glycerine at ordinary temperatures is agitated with the calculated quantity of sulphur chloride, S₂Cl₂, or the heavy sulphur chloride is covered by the lighter glycerine, and the following reaction induced by gentle heating:



and so regulated by air agitation that the main decomposition takes place at 50 to 70°C. After some time it is heated to higher temperatures to complete the reaction. In this way 80 to 90 per cent of the glycerine used is converted into monochlorohydrine directly, the rest consisting of unchanged glycerine, with small quantities of dichlorohydrine, which are for the most part removed on evaporating the water. Polymerized glycerine, which is easily formed by the hydrochloric acid chlorination in an autoclave, and which makes inconvenient the purification of the nitroglycerine made from the crude product does not appear in this process. After separation of the sulphur formed in the reaction, as well as the resinous products, the separation of which is promoted by dilution, the crude product is concentrated in a vacuum, i.e., the water is driven off. It forms a brown liquid having a specific gravity of about 1.33, or 35° Bé, somewhat less viscous than glycerine, and which is usually nitrated directly. By-products of this process are sulphur, sulphur dioxide and hydrochloric acid. The commercial yield amounts to about 110 kg. of chlorohydrine per 100 kg. of glycerine, the theoretical being 120.1 kg.

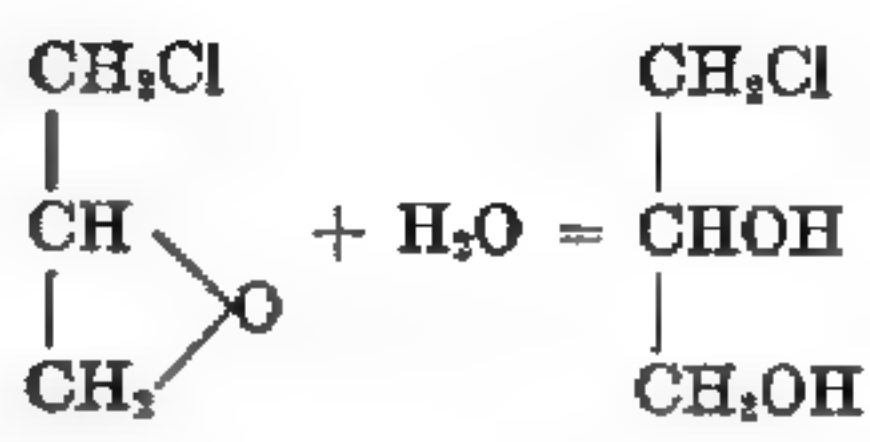
According to French patent 352750, issued to the Westfälisch-Anhaltische

¹ The process was worked out by the Dynamit-A.-G.

Sprengstoff-A.-G., hydrochloric acid gas is passed into glycerine warmed to 70 to 100°C., forming mainly the α-monochlorohydrine, with some β-monochlorohydrine. After the reaction is complete the chlorohydrine can be distilled in vacuo from the unchanged glycerine.

According to German patents 197308 and 197309, issued to Böhringer and Sons, in the manufacture of monochlorohydrine from glycerine and aqueous or gaseous hydrochloric acid it is of advantage to add organic acids like glacial acetic acid in small quantities, as catalysts to favor the reaction.

Only the α-monochlorohydrine is formed on boiling epichlorohydrine with water:



a process which has no commercial importance. β-monochlorohydrine is formed by the addition of hypochlorous acid to allyl alcohol.

Pure monochlorohydrine is a water-white, syrupy liquid, very slightly aromatic in odor, with a somewhat burning, bitter taste and a lower viscosity than glycerine. The time taken for 5 cc. to run out of a 10 cc. pipette at 20°C. is as follows:

Glycerine.....	13 minutes
Monochlorohydrine.....	1 minute 40 seconds
Dichlorohydrine.....	8½ seconds
Water.....	4½ seconds

so that the viscosities of water, dichlorohydrine, monochlorohydrine and glycerine have the relation of 1:2:22:173.

Specific gravity of the α-compound.....	1.338	at 15°C.
Specific gravity of the β-compound.....	1.328	at 15°C.
Boiling point of the α-compound.....	117.5°	at 12 mm.
Boiling point of the α-compound.....	130°	at 18 mm.
Boiling point of the α-compound.....	216°	at 750 mm.
Boiling point of the β-compound.....	146°	at 18 mm.

Monochlorohydrine is miscible in all proportions with water, alcohol and ether. As would be expected from its close relationship to glycerine, it is strongly hygroscopic, and absorbs up to 20 per cent water from moist air.

No particular quality specifications are placed on the commercial product, aside from the absence of water, hydrochloric acid and

glycerine polymerization products, which form emulsions in washing the nitroglycerine made from it, and so hinder the separation from the wash waters. The explosive plants usually make this product themselves at their own plants, and nitrate the concentrated crude product without further purification.

Manufacturing processes. Regarding the manufacturing processes little remains to be said on account of the exact analogy to the manufacture of nitroglycerine. The required quantity of nitric acid is naturally less per unit of weight of monochlorohydrine than in the nitration of equal amounts of glycerine. This naturally depends upon the relation between chlorohydrine and glycerine in the chlorinated material to be used.

The evolution of heat is less on account of the smaller quantity of water formed per unit of weight of the chlorohydrine. The nitration is therefore relatively more rapid. The separation of the explosive oil from the spent acid is rapid and sharp, the lower specific gravity of the dinitrochlorohydrine as compared to nitroglycerine being of considerable influence. However, an after-separation is obtained, just as with nitroglycerine.

On the whole, the manufacture can be considered as less dangerous than that of nitroglycerine because the dinitrochlorohydrine is less sensitive to shock, friction and heat than the former, and on gentle heating shows less tendency toward a violent decomposition. The smaller overloading of the molecule by nitric acid radicals makes it more stable than the nitroglycerine molecule.

Example of nitration of pure monochlorohydrine. One hundred parts of monochlorohydrine were introduced into 450 parts of a mixed acid composed of 40 per cent HNO_3 and 60 per cent H_2SO_4 at 10 to 15°C. with cooling and agitation. There was obtained 161 parts of neutral dinitrochlorohydrine, the theoretical being 181.45 parts, or 89 per cent of theory, as well as 360 parts of a spent acid containing 16.6 per cent HNO_3 , 75 per cent H_2SO_4 and 8.4 per cent H_2O . The solubility of dinitrochlorohydrine in this spent acid is very small, amounting to only 1.9 parts in 100 parts of the acid. The nitrogen content of the dinitrochlorohydrine was 13.86 per cent, the theoretical being 13.97 per cent.

In actual practice the yields obtained with glycerine-chlorohydrine mixtures containing 10 to 20 per cent glycerine are 165 to 175 per cent of the chlorinated material used. The oil obtained naturally

contains a higher per cent of nitroglycerine than the raw material does of glycerine.

Physical and chemical properties. In a pure condition nitrochlorohydrine is a water-white liquid with a slightly spicy, aromatic odor, less viscous than nitroglycerine. The time taken for 5 cc. to run out of a 10 cc. pipette at 20°C. is as follows:

Water.....	5.0 seconds, or 100 per cent
Dinitrochlorohydrine.....	7.0 seconds, or 155 per cent
Nitroglycerine.....	12.5 seconds, or 278 per cent

The commercial product is usually yellowish or yellowish-brown to red-brown in color. Dinitrochlorohydrine has a physiological action similar to that of nitroglycerine, and like the latter causes headache when in contact with the skin. Its specific gravity is 1.541 at 15°.

The freezing point of the pure β -form (asymmetrical) is according to Kast⁷ in agreement with the data given by Will, namely +5°C., and that of the β -form (symmetrical) +16.2°C. according to Will.

It shows a great tendency toward supercooling, and can be preserved for a long time at about -20°C. in a freezing mixture without any crystallization. Various freezing points have been observed on the commercial product.

Boiling point. The commercial product, containing mainly the α -form, boils at ordinary pressures at about 190°C. with considerable decomposition and evolution of yellow vapors, and deflagration can occur. At a pressure of 13 mm. it boils almost without decomposition at 121.5°C., and at 10 mm. at 117.5°C. The distillate has a slightly acid reaction to litmus paper.

Volatility. The volatility of dinitrochlorohydrine is moderate although appreciably higher than that of nitroglycerine. The loss in weight of 20 g. in a weighing bottle 50 mm. in diameter after 24 hours was:

	per cent
At 20°C.....	0.13
At 75°C.....	3.1
Nitroglycerine at 75°C.....	0.35

Hygroscopicity. Dinitrochlorohydrine is not hygroscopic.

Solubility. Dinitrochlorohydrine shows about the same solubility

⁷ Kast., *Spreng- und Zündstoffe*, p. 173 (1921), "The Freezing Point of Dinitrochlorohydrine."

relations as nitroglycerine, and is readily soluble in ethyl alcohol, methyl alcohol, ether, acetone, ethyl acetate, glacial acetic acid, chloroform, benzene, nitrobenzene, etc., and very slightly soluble in water, dilute acids and alkalis or carbon disulphide, benzene and paraffine oil.

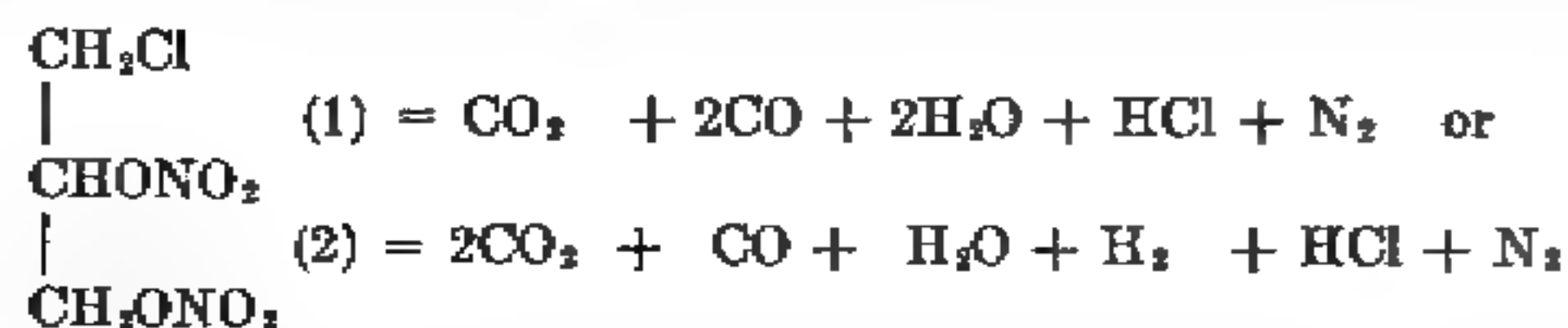
The solubility in water amounts to 2.3 grams per liter at 15°C. according to Will, and is therefore only slightly higher than nitroglycerine.

It is miscible in all proportions with nitroglycerine. The mutual solubility is so high even at low temperatures that only very small quantities of nitroglycerine can be frozen out of the mixtures at winter temperatures, even on seeding with a crystal of nitroglycerine. For this reason mixtures of dinitrochlorohydrine and nitroglycerine are very suitable for the manufacture of non-freezing or low-freezing plastic explosives. Mixtures of 75 per cent nitroglycerine and 25 per cent dinitrochlorohydrine can be considered as practically non-freezing. A mutual lowering of freezing points comes into play, the effect of which is reinforced by the very low crystallizing tendency of the eutectic mixtures.

Gelatinizing power. Pure dinitrochlorohydrine has a relatively low gelatinizing power on collodion nitrocotton. With gentle heat it forms a gelatine of little toughness, from which the oil readily exudes. On the other hand, dinitrochlorohydrine containing nitroglycerine forms good, stable gelatines with collodion nitrocotton. In practice dinitrochlorohydrine containing nitroglycerine is always used in explosives.

Chemical properties and analysis. Its chemical properties correspond to its composition as a nitric ester and a chlorine substituted product.

Explosive character. From the chemical formula and thermochemical relations dinitrochlorohydrine would be expected to be a strong explosive. It can decompose according to the following equations:



two atoms of oxygen, or 19.94 per cent, being lacking for complete combustion. With a molecular heat of formation of 87.8 calories

the heat of explosion can be calculated, with water as vapor and HCl gaseous, and at constant volume as:

- (1) 1004 Calories per kilogram
- (2) 1053 Calories per kilogram

and for water as liquid and HCl gaseous:

- (1) 1098 Calories per kilogram
- (2) 1100 Calories per kilogram

and with HCl dissolved:

- (1) 1182 Calories per kilogram
- (2) 1184 Calories per kilogram

The author found about 1140 calories in the bomb calorimeter, a value which agrees well with the calculated value, provided that a partial solution of the hydrochloric acid in the condensed water is assumed.

From the composition of the gases of explosion both reactions take place simultaneously.

Dinitrochlorohydrine is therefore a powerful explosive, but its explosion by heat or mechanical effects is much more difficult to bring about than with nitroglycerine, although on the other hand it is easily exploded by an initial impulse.

Behaviour on heating. On heating slowly small quantities in a beaker light yellow vapors are given off at 170°C., becoming more pronounced above 180°C. Finally all evaporates and decomposes without deflagration. On heating rapidly somewhat larger quantities a weak deflagration takes place at about 190°C., as with nitroglycerine.

Ignition. Dinitrochlorohydrine is difficult to ignite. If it, or explosives made from it, are ignited they burn comparatively slowly and quietly, almost without the characteristic sputtering of the nitroglycerine preparations, and without detonation. Even larger quantities of pure dinitrochlorohydrine in tin cans burn without explosion when in a fire, so that liquid dinitrochlorohydrine is permitted on German railroads in tin cans holding 25 kg., as a safe explosive for limited freight service in the 200 kg. class,⁸ while liquid nitroglycerine is absolutely excluded. As regards chemical stability it surpasses nitroglycerine appreciably. The reaction with

⁸ Supplement C of the German Railroad Regulations (1911), pp. 52 and 56.

potassium iodide-starch paper in the Abel test at 72°C. occurs after thirty minutes, but the heat test at 75°C. in a loosely covered weighing bottle is much longer than with nitroglycerine. An acid reaction occurs after ten to twelve days, and only after eighteen to twenty days do the samples decompose completely and give off yellow vapors.

Behaviour toward shock. Dinitrochlorohydrine is relatively insensitive to shock, very much more so than nitroglycerine, which is closely related to it as regards energy content and therefore gives an interesting comparison. This is partly due to its low viscosity, which permits it to be spread out in thin layers and soften the shock,⁹ while dinitroglycerine is more viscous than nitroglycerine, and in spite of its appreciably lower energy content is almost as sensitive as the latter.

Kast¹⁰ with liquid dinitrochlorohydrine obtained a drop of 10 to 20 cm. of the 2 kg. weight (liquid nitroglycerine gave 4 cm.), with the 10 kg. weight 8 to 10 cm. (liquid nitroglycerine 2 cm.). When mixed with kieselguhr these figures became 15 to 30 cm. and 6 to 8 cm., respectively (guhr dynamite with nitroglycerine gave 8 cm. and 2 cm., respectively), but he stated that while nitroglycerine detonated with a sharp report, dinitrochlorohydrine ignited only in part and with a slight report. Likewise guhr dynamite made from dinitrochlorohydrine gave a much weaker report under the falling weight test than when made from nitroglycerine. From the determination made by Will the sensitiveness to shock of the various samples differs somewhat with the degree of purity, but is always less than with nitroglycerine. He gives the sensitiveness limit with the 2 kg. weight as 35 to 80 cm. The author found values agreeing with Will when using a chemically pure dinitrochlorohydrine with a 2 kg. weight, namely, from 40 cm. up very slight partial decomposition and slight report, from 75 cm. up a somewhat more violent partial deflagration but in no case a sharp report, and even with the 10 kg. weight at 10 to 15 cm. a very weak partial decomposition.

When gelatinized with 7 per cent collodion nitrocotton pure dinitrochlorohydrine is still more insensitive, so that its low viscosity cannot be the only cause of its great insensitiveness to shock.

Dinitrochlorohydrine retains a relatively high degree of safety in handling, even when mixed with small amounts of nitroglycerine, for

⁹ Kast., *Spreng- und Zündstoffe*, p. 171 (1921).

¹⁰ Kast., *Spreng- und Zündstoffe*, p. 171 (1921).

example, 10 to 20 per cent, so that explosive mixtures containing dinitrochlorohydrine with up to 5 per cent of the total composed of nitroglycerine are permitted on German railroads without restriction.

Detonation by initiation; sensitiveness; explosive effect. Dinitrochlorohydrine, due to its low viscosity, which propagates the wave of detonation relatively easily through the liquid, is very sensitive to an initial impulse, and develops a high strength even with the weakest blasting cap, a No. 1. Ten grams of it in the Trauzl lead block under water tamping give:

With a Number 1 cap.....	cc. 380
With a Number 8 cap.....	475

so that a No. 1. cap gives 80 per cent of the effectiveness of a No. 8 cap, while with nitroglycerine this ratio is 32:100.

With an expansion of 475 cc. dinitrochlorohydrine gives 79 per cent of the expansion given by nitroglycerine, which is 600 cc., while the heats of explosion, or energy contents, are 1140 and 1595 Calories respectively, or as 71.4:100. The velocity of detonation of liquid dinitrochlorohydrine in small quantities and under slight confinement must be greater than that of nitroglycerine.¹¹

Crusher effect. In the Hess crusher test 100 grams of liquid dinitrochlorohydrine in a sheet metal container crushed a 65 mm. high lead block 17.5 mm. Dinitroglycerine compressed it 21 mm. The crushing effects of dinitrochlorohydrine and of dinitroglycerine are therefore as 83.3:100, that is, nearly in the ratio of the heats of explosion, 87.5:100. Dinitroglycerine has 1304 Calories, dinitrochlorohydrine 1140 Calories, the average of the two theoretically possible explosion equations.

Velocity of detonation. In explosive mixtures pure dinitrochlorohydrine gives lower velocities of detonation than nitroglycerine. The mixtures of the two in practical explosives give velocities which are not much below those given by pure nitroglycerine explosives. (See table 7.)

The non-freezing explosives in which 20 to 30 per cent of the nitroglycerine is replaced by dinitrochlorohydrine show no appreciable

¹¹ This is true only of small quantities and light confinement. With a greater diameter and strong confinement, nitroglycerine can develop a very high velocity of detonation, which is not attained by dinitrochlorohydrine.

reduction in strength as compared to those made from pure nitroglycerine. The figures given for the various comparisons of nitroglycerine deviate somewhat from one another. This is because they were determined at various times with various lead blocks. Values are only comparable if obtained simultaneously with lead blocks made from the same melt, which fact has been taken into consideration in determining the figures for the different esters.

TABLE 7
Explosive action of mixtures (lead block expansion)

OF	IN 75 PER CENT GURR DYNAMITE	IN 92 PER CENT BLASTING GELATINE	IN 65 PER CENT GELATINE DYNAMITE
	cc.	cc.	cc.
Dinitrochlorohydrine.....	240*	440†	325‡
Nitroglycerine.....	305*	560†	390‡
Nitroglycerine containing 20 per cent dinitrochlorohydrine.....	300	540	380
Nitroglycerine containing 30 per cent dinitrochlorohydrine.....	295	515	375

Heat of explosion, 71.4:100.

* 80:100.

† 78.5:100.

‡ 83:100.

Monochlorohydrine mononitrate (mononitrochlorohydrine)



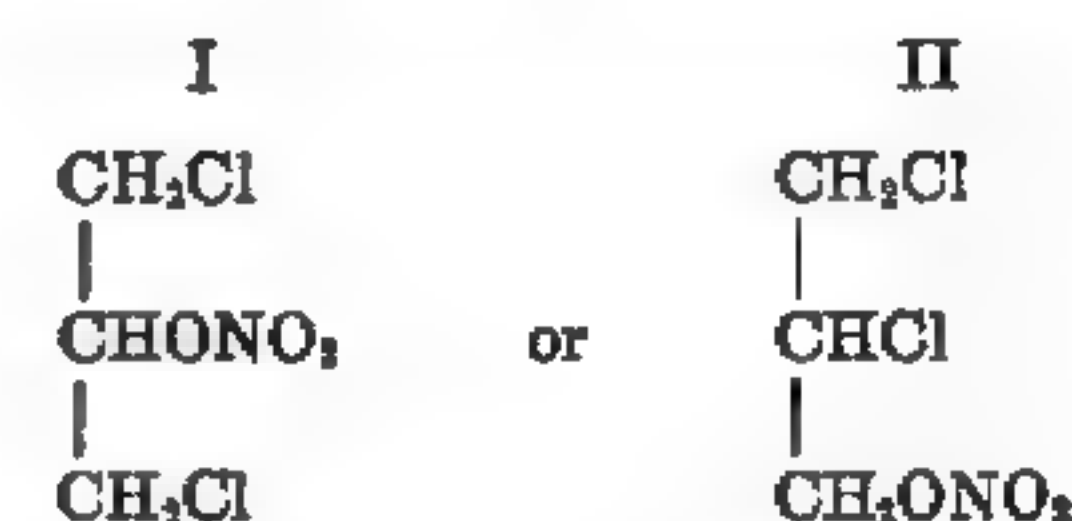
Monochlorohydrine mononitrate is to be considered as the intermediate product in the formation of dinitrochlorohydrine from monochlorohydrine, and the above three isomeric forms are possible.

It is obtained by adding monochlorohydrine to a moderate amount of nitric acid, for example three times its weight of 80 per cent HNO₃, diluting with water, neutralizing and extracting with ether. The isomers 1 and 2, as well as dinitrochlorohydrine are also formed by the action of nitric acid on epichlorohydrine. It is a colorless oil,

more viscous than dinitrochlorohydrine, and more easily soluble in water on account of the presence of an hydroxyl group. At a pressure of 10 mm. it distills at 110 to 115°C. without decomposition. It gelatinizes collodion nitrocotton when warm.

Its nitrogen content is 9 per cent. It does not detonate under the falling weight, but in spite of its strongly negative oxygen balance of -46.3 per cent it can be given an explosive decomposition by initiation under certain conditions. It is of no importance in the explosive art.

Dichlorohydrine nitrate (nitrodichlorohydrine)



Even this product, which is formed by a smooth reaction from the two dichlorohydrines which boil at ordinary pressures at 174°C. (symmetrical) and 182 to 183°C. (asymmetrical), by esterification with mixed acids or strong nitric acid, has been proposed as a means of reducing the freezing point of nitroglycerine explosives, in spite of its very low explosive strength and unfavorable properties.¹²

Its low viscosity, poor gelatinizing powers, and consequent easy exudation, high volatility, high chlorine content and low explosive strength are serious disadvantages as compared to dinitrochlorohydrine, and it has no particular advantages. It may have found a practical application in mixtures with dinitrochlorohydrine. Nothing is known regarding its use as a sole addition to nitroglycerine explosives.

Preparation. One hundred grams of dichlorohydrine was put into 200 grams of a mixture of 40 per cent HNO₃ and 60 per cent H₂SO₄ with cooling, although the development of heat is only slight. The ester soon separated on the surface of the liquid, and was collected and neutralized just like nitroglycerine or dinitrochlorohydrine. The yield was 127.5 grams, or 94.4 per cent of theory (134.9 grams). The nitrogen content by nitrometer was 8.00 per cent, calculated 8.05 per cent. The calculated chlorine content was 40.81 per cent.

¹² British patent 17891 (1906), and German patent 197404 (1905).

Properties. Nitrodichlorohydrine is a water-white, very mobile liquid, very similar to dinitrochlorohydrine but having a pronounced spiciness, aromatic odor, less viscous and more volatile than the latter.

Viscosity. The time required for 5 cc. to run out of a 10 cc. pipette at 20°C. was:

	seconds
Nitroglycerine.....	12.5
Dinitrochlorohydrine.....	7.0
Nitrodichlorohydrine.....	5.0
Water.....	4.5

Volatility. The loss of weight of 20 grams in twenty-four hours in an open glass 50 mm. in diameter is shown in table 8. The specific gravity at 15°C. is 1.45. It distills without decomposition at 88°C. under 15 mm. pressure, but at ordinary pressures at 176°C.,

TABLE 8
Loss of weight of 20 grams of nitroglycerine in twenty-four hours

	NITRODICHLO- HYDRINE	DINITROCHLO- HYDRINE	NITRO- GLYCERINE
	per cent	per cent	per cent
At 75°C.....	14.5	3.1	0.35
At 20°C.....	2.6	0.13	0.00

with slight decomposition, yellow coloration and evolution of nitrous vapors. On heating it splits off nitrous acid at 170 to 180°C., and the liquid volatilizes in small quantities without deflagration.

Chemical stability. On account of the slight degree of loading of the molecule with nitric groups its chemical stability is very high. It can be stored in a loosely covered weighing glass at 75°C. for many days without decomposition. It is insoluble in water, but on the other hand it is dissolved by the same solvents as dissolve nitroglycerine, and it mixes with nitroglycerine.

Gelatinizing powers. Nitrodichlorohydrine does not gelatinize collodion nitrocotton and therefore tends to cause exudation from gelatinized explosives.

Explosive character. It is absolutely insensitive to shock, and stands at the limit of explosibility, since an explosive decomposition can hardly be effected even by initiation. In a liquid condition it is not exploded by a No. 8 cap in the lead block with water tamping,

merely giving a partial decomposition and evolution of carbon without any expansion of the block.

On the other hand, 10 grams of it, mixed with 3 grams of kieselguhr to form a moist powder, gives a slight explosion in the lead block with a No. 8 cap, and an expansion of 75 cc. net, from which 30 cc. must be deducted to allow for the action of the cap itself. Hydrochloric acid and phosgene are among the products of explosion.

Nitrodichlorohydrine lacks 41.4 per cent oxygen for complete combustion to CO₂, H₂O, HCl and N₂. If a decomposition according to the equation:



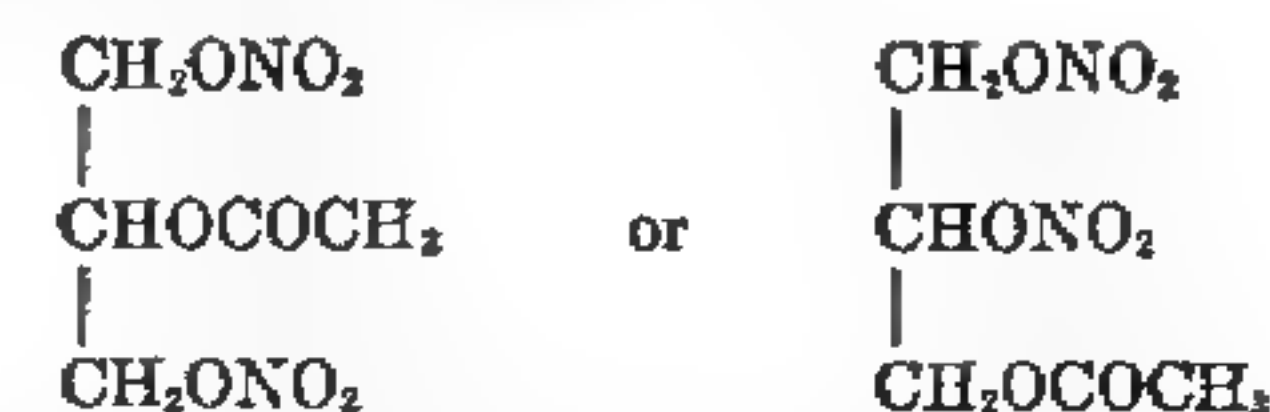
or



is assumed, this reaction has a positive heat of 259 or 440 Calories¹³ per kilogram, with water as vapor and at constant volume and thus can theoretically be explosive. The molecular heat of formation is 81.9 Calories. However, the sensitiveness is extraordinarily low, the liquid nature of the material contributing. On the other hand, compare the behaviour of ethyl nitrate, which in spite of its appreciably lower oxygen balance of -61.54 per cent, can be detonated with brisance even when liquid.

ACETYLDINITROGLYCERINE (DINITROACETIN)

This is the product of acetylation of dinitroglycerine, or the nitric ester of glycerine monoacetin:



and belongs to the explosive nitric esters of glycerine which have been proposed as addition agents to lower the freezing point of nitroglycerine.¹⁴ It has the advantage over dinitroglycerine in being insolu-

¹³ Or 495 Calories per kilogram with water as liquid.

¹⁴ Z. Schiess- u. Sprengstoffw. (1907), p. 21; Dr. Vezio Vender, "Ueber praktisch ungefrorenbare Pulver und Sprengstoffe," VI Internat. Kongress angew. Chem., Rome (1906), II. 582.

ble in water, but as compared to dinitrochlorohydrine it has the disadvantage of expensive manufacture and low explosive strength. For this reason it reduces the brisance of nitroglycerine preparations containing it to a considerable extent. Moreover, since its ability to form eutectic mixtures with nitroglycerine which will not freeze is very slight, much smaller than that of dinitrochlorohydrine, it seems to have found very little application. The product was used under the name of nitroacetin or nitroformin (formyldinitroglycerine, which see) for the manufacture of dynamite and blasting gelatine by the Società Italiana di prodotti esplodenti (*loc. cit.*).

Preparation. 1. *From glycerine monoacetate and mixed acid.*¹⁵ According to Vender the nitration of monoacetin by ordinary mixed acid, as in the manufacture of nitroglycerine, gives mainly nitroglycerine in very poor yields and only a small amount of nitroacetin. On the other hand, mixed acids containing considerably more nitric acid than sulphuric acid give pure nitroacetin.

Example. One hundred parts of monoacetin were put into a mixture of 250 parts of nitric acid of a specific gravity of 1.51 and 62.5 parts of oleum containing 25 per cent free SO₃ at a temperature not exceeding 25°C. The charge was poured into water, the oil washed with first cold, then warm 70 per cent soda solution, and about 159 parts of dinitroacetin obtained, a yield of 95 per cent of theory, which is 167.2 parts.

2. *From dinitroglycerine and acetic anhydride.* Dinitroacetin can also be obtained by acetylation of dinitroglycerine with an excess of acetic anhydride by heating a mixture of one part of dinitroglycerine with three parts of acetic anhydride for four to six hours in boiling water, driving off the excess of acetic anhydride in a vacuum at 40 to 50°C., treating the oil obtained with a warm soda solution and finally with water, some unchanged dinitroglycerine being obtained at the same time.

The theoretical yield is 123.1 parts of dinitroacetin from 100 parts of dinitroglycerine. The actual yield obtained was about 90 per cent of theory. The nitrogen content by nitrometer was 12.40 per cent, the calculated being 12.50 per cent. This latter process can only be considered for use in the laboratory.

¹⁵ According to Dr. V. Vender, *loc. cit.*, also German patent 209943 (1906); British patent 9791 (1906); French patent 372267 (1906); Swiss patent 50836 (1910); United States patent 1029519 (1912).

Properties. In a pure condition dinitroacetin is a colorless and odorless oil, having a specific gravity of 1.412 at 15°C. according to the author, 1.45 to 15°C. according to Vender (*loc. cit.*) which does not freeze even at -20°C., and boils under 15 mm. pressure at 147°C., but not without some decomposition.

Volatility. The volatility is less than that of dinitrochlorohydrine, but somewhat higher than that of nitroglycerine and dinitroglycerine. The loss of weight in twenty-four hours at 75°C. was 1.4 per cent.

Viscosity. Dinitroacetin is less viscous than dinitroglycerine, but somewhat more so than nitroglycerine. The time taken for 5 cc. to run out of a 10 cc. pipette at 20°C. was:

	<i>seconds</i>
Nitroglycerine.....	12.5
Dinitroacetin.....	15.5
Dinitroglycerine.....	26.0

Solubility. It is insoluble in water, but dissolves easily in alcohol, ether, acetone, and concentrated nitric acid, and is miscible in all proportions with nitroglycerine, which makes it capable of producing low-freezing explosive oil mixtures with the latter.

Gelatinizing powers. Dinitroacetin gelatinizes collodion nitrocotton, and even gun cotton, at room temperatures.

Explosive character; Explosive effects

Acetyldinitroglycerine (dinitroacetin) lacks six atoms of oxygen per molecule for complete combustion, or 100 parts by weight lack 42.86 parts of oxygen, so that its oxygen deficiency is 42.86 per cent. However, it has considerable explosive strength, decomposing according to the following equation:



giving a heat of explosion of 657 Calories per kilogram with water as vapor and at constant volume.¹⁶ The molecular heat of formation is 165.6 Calories. It is therefore far below dinitroglycerine and dinitrochlorohydrine, and as compared to the latter has the advantage of producing gases on explosion which contain no hydrochloric acid. Its energy content is only 44.7 per cent of that of nitroglycerine.

Moreover its sensitiveness to an initial impulse is only slight.

¹⁶ Or 715 Calories per kilogram with water as a liquid.

According to determinations by the author 10 grams of it as a liquid in the lead block with a No. 8 cap gave only about 200 cc. net expansion, which is low in comparison to the energy content of 657 Calories. The value of 450 cc. given by Vender apparently refers to a product containing nitroglycerine, because it is not in agreement with the energy content and viscosity of the product.

On slow heating in a glass tube decomposition begins at 160°C., with a yellow coloration and evolution of nitrous vapors. At 170 to

TABLE 9
Sensitiveness of kieselguhr mixtures

	NITROGLYCER- INE GUHR DYNAMITE	DINITROACETIN GUHR DYNAMITE
	cc.	cc.
Lead block expansion.....	320	202
Ratio.....	100	63

TABLE 10
Replacement of nitroglycerine by dinitroacetin to reduce brisance

	NITROGLYCER- INE GUHR DYNAMITE	80/20 NITRO- GLYCERINE- DINITROACETIN GUHR DYNAMITE
	cc.	cc.
Lead block expansion.....	320	275
Ratio.....	100	86
Energy content ratio.....	100	89

180°C. a vigorous decomposition sets in. When heated rapidly on platinum foil it ignites and burns rapidly with very slight deflagration.

Stability. The stability of the product obtained by acetylation of dinitroglycerine and stabilized in the usual way is less than that of nitroglycerine. The Abel test reaction occurs in about ten minutes. At 75°C. the oil is acid after twenty-four hours and shows slight yellow vapors.

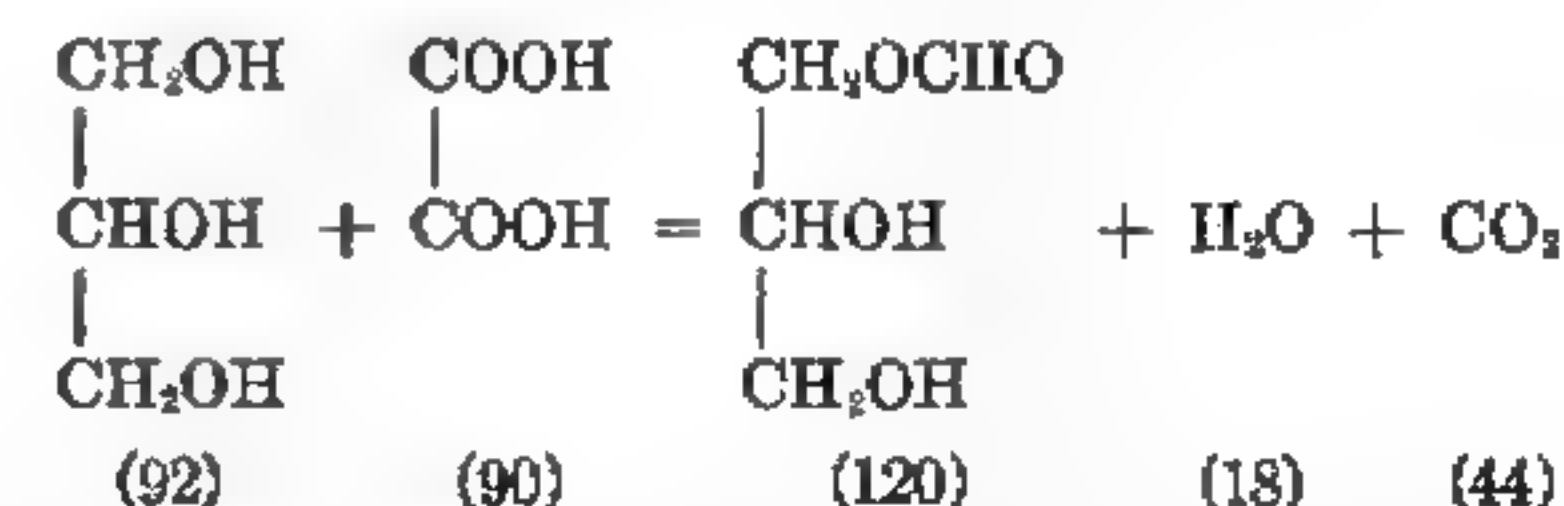
It is very insensitive toward shock, and in this respect does not differ appreciably from dinitrochlorohydrine.

Explosive action in mixtures. In a gelatinized condition dinitroacetin is even more insensitive than when a liquid. A gelatine con-

taining 92 per cent dinitroacetin and 8 per cent collodion nitrocotton gave only about 145 cc. net expansion in the lead block, while nitroglycerine gave 570 cc. On the other hand, kieselguhr mixtures show a higher sensitiveness, as is shown by table 9. Correspondingly the brisance of nitroglycerine explosives containing a 20 per cent replacement of nitroglycerine by dinitroacetin to render them low-freezing is not much reduced. (See table 10.) Similar relations exist for gelatine dynamite and blasting gelatine.

FORMYLDINITROGLYCERINE (DINITROFORMIN)

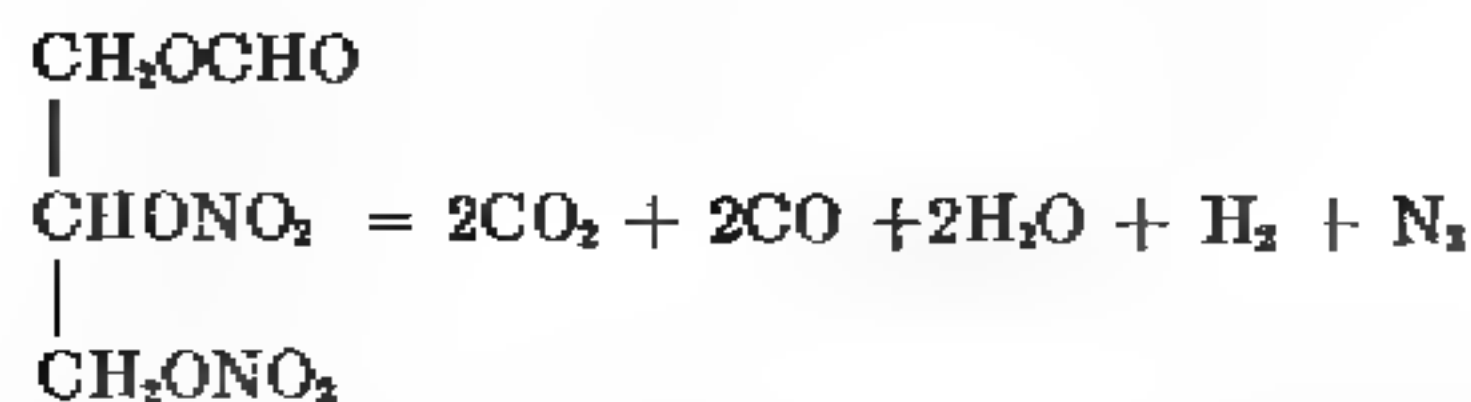
This explosive glycerine ester, like dinitroacetin, was proposed by the Italian Dr. Vezio Vender as an addition to nitroglycerine to make non-freezing oil mixtures.¹⁷ Although its structural formula shows it to surpass dinitroacetin in explosive strength, on account of its rather high cost of manufacture it has attained hardly any commercial importance. Vender made it from oxalic acid. Glycerine monoformin is formed from glycerine and oxalic acid according to the following equation:



Therefore about 1 part of anhydrous oxalic acid is required for 1 part of glycerine to form monoformin. Vender heated a mixture of 2 parts of glycerine with 1 part of anhydrous oxalic acid first to 100°C., then for twenty hours at 140 to 150°C., and nitrated the resulting product directly with mixed acid. The oil, washed with dilute soda solutions, is a mixture of 70 per cent nitroglycerine and 30 per cent dinitroformin. It can be used directly to make non-freezing explosives. Dinitroformin does not appear to have as yet been isolated in a pure state.

Explosive Character. Dinitroformin lacks only 3 atoms of oxygen per molecule for complete combustion. Its oxygen balance is therefore -22.9 per cent. On explosive decomposition according to the following equation:

¹⁷ See preceding chapter.



it gives 1009 Calories with water as vapor and at constant volume, or 1099 Calories per kilogram with water as a liquid. Its heat of explosion is therefore about equal to that of dinitrochlorohydrine and 68 per cent of that of nitroglycerine. A mixture of 70 per cent nitroglycerine and 30 per cent dinitroformin has therefore about 90 per cent of the energy content of nitroglycerine, and must approximate the explosive strength of the latter very closely.

CHAPTER XVI

THE NITRIC ESTER OF POLYMERIZED GLYCERINE

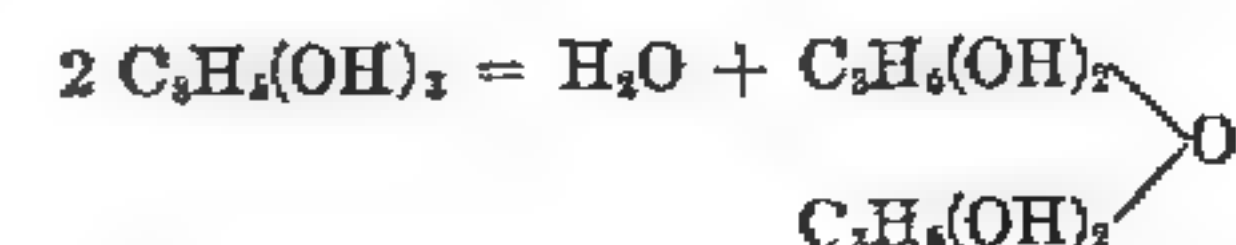
TETRANITRODIGLYCERINE

The use of a polymerized glycerine to produce non-freezing explosive oils was first proposed by Wohl in German patent 58957 (1890). He heated glycerine with small quantities of concentrated sulphuric acid to 130 to 160°C., the anhydride formation depending upon the amount of acid present and the time of heating. The mixture obtained, containing glycerine, diglycerine and polyglycerine, was then nitrated to produce a low-freezing explosive oil.

On testing out this process Will,¹ by using 0.5 to 5 parts of sulphuric acid per 100 parts of glycerine, obtained a mixture strongly contaminated with by-products, which on nitration gave an explosive oil which could not be purified.

Will and Stöhrer² polymerized glycerine by boiling gently at 290 to 295°C. for seven to eight hours without adding any acid, taking care that the water formed distilled off, while the components boiling higher were condensed and returned. Later it was found that small additions, e.g., about 0.5 per cent of alkalis, soda or alkali sulphides catalytically favored the splitting of water and formation of the polymerization products.

In this way up to 60 per cent of the glycerine was converted to diglycerine:



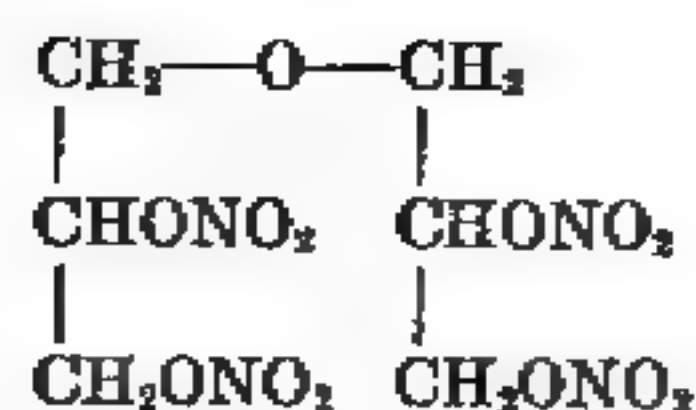
and only small quantities of polyglycerine were formed, e.g., 4 to 6 per cent, depending upon the heating.

The product obtained was then nitrated or previously mixed with

¹ *Z. Schiess- und Sprengstoffw.* (1906), p. 231.

² *Z. Schiess- und Sprengstoffw.* (1906), p. 231.

sufficient glycerine so that on nitration it would give an oil with a sufficiently high content of tetranitrodiglycerine:



to reduce the freezing point correspondingly.³ Mixtures of 70 to 80 per cent nitroglycerine and 30 to 20 per cent tetranitrodiglycerine can be considered as practically non-freezing.

According to Will even a content of 20 to 25 per cent diglycerine in the glycerine prevents the freezing of explosive oils obtained from such mixtures at winter temperatures in Germany.

Will separated the polymerized mixture by fractional distillation at 8 to 10 mm. pressure, the unchanged glycerine passing over between 160 to 220°C., the diglycerine at 220 to 270°C., and the higher polymers above 270°.

Diglycerine. This is obtained in a pure state by repeated distillation in a vacuum. It is a water-white, very viscous, sweet-tasting and very hygroscopic liquid, easily soluble in water, boiling at 245 to 250°C. under 8 mm. pressure without decomposition, having a specific gravity of 1.33 as compared to 1.26 for glycerine. The viscosity is about eleven times that of glycerine.

Manufacture of tetranitrodiglycerine

Diglycerine can be readily nitrated by mixed acids, just like glycerine, the nitration requiring a quantity of nitric acid like that required to form dinitroglycerine from glycerine.

The nitration requires a somewhat smaller quantity of the same mixed acid than the nitration of glycerine. The diglycerine is warmed up to about 50 to 60°C. to reduce its viscosity somewhat. The separation is slower than with nitroglycerine. Common salt solutions are used for the stabilization, to prevent emulsions which form readily. The washed product retains moisture rather firmly and is more difficult to obtain dry than is nitroglycerine.

Yields. From 100 parts of diglycerine about 168 parts of tetra-

nitrodiglycerine, or 81 per cent of theory, (208.4 per cent), is obtained. The nitrogen content in the nitrometer is 15.98 per cent, the calculated being 16.18 per cent.

Properties. Tetranitrodiglycerine is a very thick oil, insoluble in water and not hygroscopic. It dissolves readily in alcohol, ether, and other organic solvents. Up to the present time it has never been crystallized by cooling.

Gelatinizing powers. The gelatinizing powers of pure tetranitrodiglycerine on collodion nitrocotton are insufficient for practical purposes, but its mixtures with nitroglycerine, while gelatinizing more slowly than nitroglycerine alone, nevertheless give satisfactory gelatines.

Explosive character. Tetranitrodiglycerine behaves like nitroglycerine and explodes readily by shock or initiation. It is some-

TABLE 11

EXPLOSIVE EFFECT	75 PER CENT NITROGLYCER- INE GUEB DYNAMITE	75 PER CENT TETRANITRODI- GLYCERINE GUEB DYNAMITE
	cc.	cc.
Expansion.....	320	274.0
Ratio.....	100	85.6
Energy content ratio.....	100	85.9

what less sensitive to shock than nitroglycerine, and about the same as dinitroglycerine. Under the 2 kg. weight explosion occurs at 8 to 10 cm.

The molecule lacks 4 atoms of oxygen for complete combustion. The oxygen balance is therefore -18.5 per cent, as compared to dinitroglycerine with -17.6 per cent. On explosive decomposition according to the following equation:



the heats of explosion amount to 1371 and 1370 respectively per kilogram with water liquid and at constant volume, assuming a molecular heat of formation of 165.1 Calories for tetranitroglycerine. (See table 11.) This is almost a perfect agreement.

³ German patent 181754 (1906), and British patent 6314 (1906).

Practical importance. Tetranitrodiglycerine, or its mixtures with nitroglycerine, have the advantage over dinitrochlorohydrine of forming gases on explosion which are free from hydrochloric acid, over dinitroglycerine the advantage of insolubility in water, but on the other hand the safety in handling is not appreciably higher than that of nitroglycerine. The simple manufacture of the raw material, the glycerine-diglycerine mixture, by the mere heating of glycerine, is an advantage.

However, appreciable practical difficulties were encountered at first. The separation and purification of the diglycerine is difficult and expensive on account of the high vacuum and high temperatures required. Steam distillation, as with glycerine, is not allowable.

On the other hand, the original polymerization products contain most of the impurities which cause the formation of emulsions and a slow separation of the oil from the wash waters in direct nitration, separation and stabilization. These troubles can be reduced by the use of salt solutions in the stabilizing washes.⁴ The commercial nitration is rendered difficult by the greater viscosity of the glycerine-diglycerine mixture.

In Germany for these reasons the process has been very little used on a commercial scale, and has not been able to overcome the competition of the easily produced dinitrochlorohydrine. In the United States the process seems to have been used for some time.⁵

⁴ These troubles are not merely reduced, but completely avoided by the use of salt solutions in washing. The use of such salt solutions is universal in the United States for tetranitrodiglycerine and has been since it was introduced.—TRANSLATOR.

⁵ For about fourteen years to a large extent.—TRANSLATOR.

CHAPTER XVII

THE HOMOLOGOUS NITRIC ESTERS

METHYL NITRATE



Of the nitric esters of the primary alcohols of the fatty series, methyl nitrate is theoretically the most important on account of its high explosive properties and high energy content, which is on a par with nitroglycerine, to which it is stoichiometrically related very closely, as can be seen from table 12. Practically, it has had no importance as an explosive up to the present time on account of its great volatility, as well as on account of the danger from fire or explosion of the liquid or vapors in increasing the risk in commercial manufacture or use.

According to Meyer-Jakobsen it has been made commercially for some time for use in the dye industry for methylation, but on account of several disastrous explosions its manufacture was given up.

*Preparation.*¹ Methyl nitrate, like ethyl nitrate, can be obtained by careful distillation of the proper alcohol with moderately strong nitric acid, e.g., of a specific gravity of 1.4. It can also be obtained, like nitroglycerine and nitroglycol, by putting the alcohol into a mixture of concentrated nitric and sulphuric acids, with good yields, while ethyl alcohol and other mono- and polyvalent alcohols containing methyl or methylene groups readily undergo oxidation in such a case.

Example. One hundred grams of pure, anhydrous methyl alcohol was added gradually to 630 grams of a mixed acid containing 40 per cent HNO_3 and 60 per cent H_2SO_4 , contained in a spherical glass vessel having three openings for a stirrer, thermometer and inlet, the mixture being well cooled, mechanically stirred and maintained at 0 to 10°C., the operation taking twenty-five minutes. Agitation by compressed air is out of the question on account of the volatility of the ester. The ester separated rapidly in a funnel. It was digested

¹ *Beilstein*, IV. Auflage I, p. 284.

with cold water and then neutralized with a soda solution. There was obtained 196 grams of neutral methyl nitrate, or 81.5 per cent of theory (240.6 grams).

Properties. Methyl nitrate is a colorless, very mobile liquid of a high volatility and strongly aromatic odor, somewhat resembling chloroform. The vapors cause headache when inhaled. It is somewhat less viscous than water, and has a specific gravity of 1.21 at 15°C. At ordinary pressures it distils at 65°C. without decomposition. Water dissolves it only slightly at room temperatures. One hundred cubic centimeters of water at 20°C. dissolve 3.85 grams of methyl nitrate. Collodion nitrocotton is dissolved, forming a gelatine, from which the methyl nitrate evaporates very easily.

TABLE 12
Relation of methyl nitrate to nitroglycerine

	METHYL NITRATE	NITROGLYCERINE
Molecular weight.....	77	227
Composition:	per cent	per cent
C.....	15.8	15.86
H.....	3.9	2.20
O.....	62.3	63.44
N.....	18.2	18.50
	100.0	100.0

Explosive character. The thermochemical relations of methyl nitrate have already been determined by Berthelot.² The explosive decomposition is possibly along the line of the following equations:



The molecule lacks one atom of oxygen for complete combustion. The oxygen balance is therefore -10.39 per cent.

Based on a molecular heat of formation of 39.6 Calories for methyl nitrate Berthelot calculated for 1 kg. of this material at constant

² Berthelot; *Sur la force des matières explosives*; also Berthelot; *Ann. chim. et de physique*, 6, p. 556 (1885), and 23, p. 485 (1891).

volume and with water liquid a heat of explosion of 1609 Calories according to Formula 1, and 1616 Calories according to Formula 2. Methyl nitrate has therefore a somewhat higher energy content than nitroglycerine (1595 Calories), and this makes itself evident also by a slightly higher explosive action. When shot in the lead block with water tamping:

10 grams methyl nitrate gives.....	615 cc. expansion
10 grams nitroglycerine gives.....	600 cc. expansion

The expansions are as 102.5:100. The heats of explosion are as 101.0:100, or a satisfactory agreement.

When mixed with kieselguhr or gelatinized with collodion nitrocotton it shows about the same explosive effect on the lead block as nitroglycerine, namely 320 and 565 cc.

Sensitiveness. Methyl nitrate is extremely sensitive to an initiating impulse, and when shot with a No. 1 cap under water tamping, it gives approximately the same effect as with a No. 8 cap, in contrast to nitroglycerine, which is more difficult to detonate.

	Methyl Nitrate	Nitroglycerine
Blasting cap No. 1..	520 cc. (84.5 per cent)	190 cc. (32 per cent)
Blasting cap No. 8..	615 cc. (100 per cent)	590 cc. (100 per cent)

or after deducting 30 cc. for the No. 8, and 5 cc. for the No. 1 cap:

Blasting cap No. 1...	515 cc. (88 per cent)	185 cc. (33 per cent)
Blasting cap No. 8...	585 cc. (100 per cent)	560 cc. (100 per cent)

The crusher test also shows similar relations, which were obtained with 100 grams of the liquid in a sheet lead shell with walls 1 mm. thick, tamped by thin cork plates, i.e., under slight confinement:

	Methyl Nitrate	Nitroglycol	Nitroglycerine
Compression.....	24.5 mm.	30 mm.	18.5 mm.

The lower viscosities of methyl nitrate and nitroglycol as compared to nitroglycerine give higher velocities of detonation with the first two, even with a weak confinement.

The sensitiveness also is evidenced by a flame causing detonation even in a narrow space. A small amount of methyl nitrate in a beaker, when ignited by fuse containing a black powder core, sometimes gives a puff and destruction of the glass into large pieces, sometimes a brisant detonation and pulverizing of the glass to a fine powder.

In an open dish methyl nitrate ignites immediately when in contact with a flame, and burns quietly with a large, non-luminous flame. The vapors puff readily on ignition, and on heating them to 150°C. they explode. Methyl nitrate is also sensitive to shock, although less so than nitroglycerine and nitroglycol. Under a 2 kg. weight it explodes at a drop of 40 cm. Even when mixed with kieselguhr it is appreciably less sensitive than nitroglycerine.

Velocity of detonation. The velocity of detonation was determined by Berthelot³ at very small diameters. In glass tubes 3 mm. in diameter and 1 mm. wall thickness he found 1890 meters per second, and with 4.5 mm. wall thickness 2480 meters. Nitroglycerine gives only about 1500 meters per second at such small diameters. It is indeed probable that methyl nitrate at larger diameters such as 30 to 40 mm. would give velocities of detonation of far higher magnitudes, such as 6000 to 8000 m/s.

ETHYL NITRATE



The nitric ester of ethyl alcohol is also counted among the powerful explosives which can decompose with brisant effects in spite of its strongly negative oxygen balance of -61.5 per cent. Since it is readily volatile, like methyl nitrate, and has a smaller energy content than the latter, it has been of no importance as a practical explosive, but is of theoretical interest because with it there can be easily observed the phenomenon of the wave of detonation passing through an explosive with far more difficulty when it is in the liquid state than if converted into a powder.

Preparation. One hundred grams of cold nitric acid having a specific gravity of 1.41, freed from nitrous acid by treating with a few grams of urea to eliminate the last traces, is added to 75 grams of absolute alcohol. Then about one-half is distilled off on a water bath, and a mixture of 200 grams of the same nitric acid and 150 grams of absolute alcohol and some urea is added drop by drop as the liquid distills. A mixture of ethyl nitrate and alcohol comes over. This is treated with water, the separated ester neutralized by a dilute soda solution, dried and rectified.⁴ The yield is about 35 per cent of theory (198

³ *Ann. chim. et de physique*, XXIII pp. 485-503, 1891.

⁴ *Beilstein, Handbuch*, IV, Auflage, Bd. I, p. 329.

per cent of the alcohol). On bringing together ethyl alcohol and highly concentrated nitric acid or mixed acid a violent oxidation occurs, even with the best of cooling.

Properties. Ethyl nitrate is a pleasant smelling, colorless, very volatile liquid, having a boiling point of 87°C., and a specific gravity of 1.12 at 15°C. It is very slightly soluble in water, mixes with alcohol and ether, and gelatinizes collodion nitrocotton. When ignited it burns quietly with a white light.

Explosive character. The molecule lacks 3½ atoms of oxygen for complete combustion to carbon dioxide, water and nitrogen, or the oxygen balance is -61.5 per cent. However, a thermochemical calculation of the nature of ethyl nitrate shows that it is a brisant explosive of no inconsiderable energy content.

With a decomposition according to the following equation:



the heat of explosion with a molecular heat of formation of 48.5 Calories⁵ can be calculated as 712.6 Calories per kilogram for constant volume and water as vapor, or 816.3 Calories per kilogram for constant volume and water as a liquid, which is about one-half that of nitroglycerine (1485 or 1595 Calories).

Correspondingly, under the action of an initiating impulse this compound proves a brisant explosive. The lead block expansion of 10 grams of ethyl nitrate with a No. 8 copper cap was:

	cc.
In a glass tube tamped with sand.....	325
Under water tamping.....	345
Nitroglycerine, water tamping.....	590

The fact that the lead block expansion is comparatively high as compared to nitroglycerine (58:100) and also as compared to the energy contents (48:100) is apparently because ethyl nitrate, as a result of its low viscosity, has a higher initial velocity of detonation than nitroglycerine. In other words, small quantities of the less viscous ester may detonate at higher velocities than small quantities of the more viscous ones. It is known that the velocity of detonation affects the lead block test.

In any case the sensitiveness of the liquid ethyl nitrate is already

⁵ Brunswig, *Explosivstoffe* (1909), p. 5; Berthelot, *Annuaire du bureau des longitudes* (1904), p. 723.

so low that without tamping or confinement it will not detonate under the influence of a No. 8 cap. On the other hand, a brisant detonation takes place without confinement as soon as the liquid is mixed with kieselguhr and so brought into a powdery state:

Ethyl nitrate 70 grams	} In paper shell, no tamping.....	15
Kieselguhr 30 grams		
Ethyl nitrate 60 grams	} In a sheet lead shell, lightly closed by	19
Kieselguhr 40 grams		

These data point to a velocity of detonation of a magnitude of 6000 to 7000 meters per second. The conditions given are, therefore, of a special importance because in the literature a special inertness to detonation has been ascribed⁶ to the aliphatic nitric esters as compared to the rather easy detonation of the violently explosive nitro bodies of the aromatic series. Stettbacher is inclined to ascribe these apparent differences of sensitiveness to differences in the chemical constitution, ascribing⁶ to the benzene ring an appreciably higher predisposition toward explosive decomposition than to the open aliphatic chains. In this he compares crystal powders or solid bodies (nitro compounds) with liquids, and neglects the fact that the wave of detonation propagates through liquids with much more difficulty. Tests under the same conditions of aggregation show that the state influences greatly the propagation of the detonating wave, and that the chemical structure of the molecule plays only a subordinate rôle.⁷

NORMAL PROPYL NITRATE



Propyl nitrate is of theoretical importance because it makes apparent even more clearly the relations mentioned under ethyl nitrate, and will therefore be considered briefly.

Preparation. It is prepared like ethyl nitrate. Twenty-five grams of a nitric acid of a specific gravity of 1.41 is mixed with 3 grams of urea and 15 grams of normal propyl alcohol, and carefully distilled over a free flame. As the liquid passes over, a mixture of 50 cc. of nitric acid and 50 cc. of propyl alcohol and 1 gram of urea is dropped in, and distilled until 105°C. is reached.

⁶ Stettbacher, *Z. Schiess- u. Sprengstoffw.* (1919), p. 22.

⁷ Naoum, *Z. Schiess- u. Sprengstoffw.* (1920), p. 5.

The distillate, amounting to about 110 cc., consists of two layers, the lower amounting to about 40 cc. and is dilute nitric acid, the upper amounting to about 70 cc., is the ester and unreacted alcohol. The solution is salted out with common salt, giving about 51 grams of the ester, or 53 per cent of theory (175 per cent of the alcohol).

Properties. Pleasant ethereal odor, volatile, boiling at 110.5° and having a specific gravity of 1.06 at 15°C.

Explosive character. Thermochemical calculation gives, with a molecular heat of formation of 56.3 Calories, a heat of explosion of 549 Calories per kilogram with water as vapor and at constant volume, and in spite of the high negative oxygen balance of -99 per cent, predicts an explosive decomposition, assuming the following equation:



Even ammonium nitrate with only 375 Calories per kilogram shows, as is known, a brisant decomposition under a powerful initiation and an expansion of 200 cc. The liquid propyl nitrate, however, will not detonate in the lead block under water tamping. Ten grams of it with a No. 8 cap give 45 cc., or only 15 cc. more than the cap alone. On the other hand there is a violent detonation and a loud report and 230 cc. expansion if 10 grams of it and 4 grams of kieselguhr are intimately mixed to a fine powder and exploded by a No. 8 cap under sand tamping.

Therefore propyl nitrate can also detonate, and under certain conditions can assume the character of a brisant explosive. A certain parallel exists between it and the aromatic nitro compound dinitrobenzene, which with a very similar negative oxygen balance of -95 per cent can likewise detonate with a high brisance and give a similar lead block expansion of 250 cc. The energy contents of propyl nitrate and nitroglycerine are as 37:100, the expansions as 40:100, an approximate agreement.

ISOPROPYL NITRATE



Isopropyl alcohol has been made recently in large quantities by the catalytic reduction of acetone.⁸ The isopropyl nitrate obtained

⁸ And also from the gases from oil cracking stills.—TRANSLATOR.

from it has hardly attained any importance as a commercial explosive component on account of its volatility and low explosive strength. Previously it had been made only by a double decomposition of isopropyl iodide and silver nitrate. It boils at 101 to 102°C.⁹ Its preparation by direct esterification with concentrated nitric acid, mixed acid, or even by nitric of a specific gravity of 1.4, with which ethyl alcohol or normal propyl alcohol can be easily esterified, is impossible, because in the secondary position the hydroxyl group is subject to oxidation very readily by the nitric acid.

NITROGLYCOL (ETHYLENE GLYCOL DINITRATE)



The next relative of nitroglycerine among the nitric esters is ethylene glycol dinitrate, abbreviated "nitroglycol," similarly to the

TABLE 13
Chemical composition of nitroglycerine and nitroglycol

	NITROGLYCERINE	NITROGLYCOL
	<i>per cent</i>	<i>per cent</i>
C.....	15.86	15.79
H.....	2.20	2.63
O.....	63.44	63.16
N.....	18.50	18.42

commonly used term "nitroglycerine." The great similarity in chemical composition as shown by the comparison given in table 13 corresponds to a great similarity in all their explosive properties, as well as in others. Although it is just as powerful an explosive and far less dangerous to handle than nitroglycerine, up to the present time it has been little considered and used as an explosive for valid economic reasons. While nitroglycerine is obtained from glycerine, a by-product of the large soap and fat industries, or from a raw material offered by nature in enormous amounts in oils and fats and which finds a mass consumption only in the explosive and powder industries, glycol, the raw material of nitroglycol, does not occur in

⁹ *Beilstein, Handbuch*, 4 Auflage, p. 363; *Silva, Ann.*, 154, p. 256.

nature and must be first built up by several stages of synthesis from alcohol or ethylene, which is naturally rather expensive, particularly as toward the end of the synthesis, i.e., after saponification of the ethylene chloride it is then only in a condition similar to glycerine on splitting or saponification of natural fats, namely as a dilute liquor. It must then be subjected to the same manufacturing stages of concentration, salt separation, rectification, etc., as the glycerine liquors.

Nitroglycol has only one appreciable disadvantage as compared to nitroglycerine, namely a higher volatility, which naturally increases its physiological disadvantages. This can be partly overcome by corresponding ventilation devices during manufacture. For gelatine dynamite this higher volatility plays no appreciable rôle, at least not in the temperate zone. On the other hand, in explosive mixtures containing small amounts of nitroglycerine, such as ammonium nitrate explosives with 4 per cent of oil, replacement of nitroglycerine by nitroglycol has not proved satisfactory in the warm periods of the year. Also nitroglycol is hardly suited for use in smokeless powder, because its volatility, even at ordinary temperatures, does not ensure a sufficient stability of the ballistic properties of the powder.

On the other hand nitroglycol shows various overwhelming advantages over nitroglycerine, such as less tendency toward decomposition during manufacture and consequently greater safety, appreciably less sensitiveness to shock both alone and in explosive mixtures, non-freezing powers, and finally a certain although not large superiority in brisance.

The first statements in the literature regarding nitroglycol are in German patent 179789 (1904), according to which it was to be used as an addition to nitroglycerine explosives to prevent freezing, and further in English patent 12770 (1912), and in *Mém. Poudres et Salpêtres*, XVI, 73, and XVII, 175 (1912 and 1914). However, at that time there appeared to have been no commercial manufacture of nitroglycol nor any practical application of it.

Only the method of preparation by saponification of ethylene bromide by alkali carbonates was known, which naturally could not be considered for a commercial process on account of the high cost of bromine and its high atomic weight, which increased considerably the quantity of salt to be separated.

The scarcity of glycerine in Germany due to the World War turned

attention to nitroglycol as a possible substitute for nitroglycerine, and all methods of preparing it were thoroughly studied. The commercial process of synthesis of glycol from alcohol via ethylene and ethylene chloride was therefore developed, and during the war many thousands of kilos of glycol were produced, mainly by the firm of Th. Goldschmidt in Essen, and furnished the explosive industry. It was nitrated to nitroglycol, partly as such and partly in mixtures with nitroglycerine as a completely equivalent substitute for the latter in mining explosives.

Manufacture of glycol

(a) *Preparation of ethylene.* The most simple preparation of ethylene in the laboratory is by heating alcohol in definite proportions with sulphuric acid of certain concentrations. By using a 90 per cent sulphuric acid and a 90 per cent alcohol ethylene can be produced in a regular stream at a yield of 84 to 85 per cent of theory.

A part of the alcohol, about 6 per cent, is converted into carbon, which remains in the residual sulphuric acid as flakes and renders its treatment and recovery difficult. For this reason only the pyrogenic decomposition of alcohol by passing alcohol vapors over aluminium oxide at something above 350°C. has been used for the commercial production of ethylene.^{10,11}

The economy of the glycol synthesis is considerably improved if the expensive alcohol can be avoided and cheaper raw materials used as the source of ethylene. According to recent processes the carbonization of lignite or lignite tar gives a gas rich in olefines, containing up to 25 per cent ethylene, which can be separated from the other constituents by fractional condensation.¹²

Attempts have also been made to remove the 4 to 5 per cent ethylene contained in illuminating gas by adding chlorine to it, forming ethylene chloride. Since substitution of chlorine, as well as addition, takes place readily the gas plants have not been ready to place their illuminating gas at the disposal of such a process of removal of the ethylene because of the danger of contaminating the illuminating gas with traces of hydrochloric acid.

¹⁰ Ber. 36 (1894); also German patent 298931.

¹¹ In the United States ethylene is manufactured on the large scale by passing alcohol vapor over coke wet with phosphoric acid in towers. The yield is high and there is no charring. —E. E. R.

¹² German patent 369368.

(b) *Preparation of ethylene chloride.* Ethylene adds on gaseous chlorine with great ease. It is essential for the production of the purest possible ethylene chloride that the chlorine be allowed to always act upon an excess of the ethylene, the excess of ethylene being returned to the process after removal of the ethylene chloride by strong cooling. Otherwise substitution takes place, and the ethylene chloride is strongly contaminated with higher boiling compounds like trichloroethane, boiling point 114°, tetrachloroethane, $\text{CH}_2\text{Cl}\cdot\text{CCl}_2$, boiling point 135° and $\text{CHCl}_2\cdot\text{CHCl}_2$, boiling point 147°. The boiling point of ethylene chloride is 84°C.

If an excess of ethylene is used, a product is obtained at a 90 per cent yield, of which 95 per cent passes over between 80 and 100°C., and by far the greater part at about 85°C. Of the 80 to 100° fraction 85 per cent can be shown to be pure ethylene chloride by saponification to glycol. Thus, even with a deficiency of chlorine, substitution is not absolutely avoided, while by the action of an excess of bromine there is only an addition, i.e., only ethylene bromide is formed.

Unfortunately for the yields the presence of moisture is injurious. Apparently moist chlorine acts as an oxidizer very readily, and by-products are formed by the oxidation of ethylene. For this reason the gases are allowed to react in a dry state one upon the other, avoiding water or salt solutions as separating liquids. Certain contact bodies, such as stoneware supporting finely divided iron chloride, favor the reaction.

On a commercial scale ethylene dichloride has been produced according to German patent 298931 (1915) issued to the Th. Goldschmidt A.-G. in Essen, and the Oscar Matter process, in which 1 volume of chlorine mixed with 3 to 4 volumes of ethylene is passed over iron chloride or copper chloride spread out on cooling coils to regulate the temperature, the ethylene chloride formed being separated out in cooling coils, and the unconverted ethylene again returned to the circuit. The crude product is purified by fractional distillation.¹³ Its boiling point is 84°C.

(c) *Saponification of ethylene chloride to glycol.* Free alkalies split off hydrochloric acid from ethylene chloride, giving vinyl chloride, $\text{CHCl} = \text{CH}_2$, and finally acetylene. On mild saponification, on the other hand, with carbonates or still better bicarbonates, and corre-

¹³ See also Austrian patent 88625.

sponding dilution, the halogen is exchanged for hydroxyl, and glycol is obtained at a good yield.

According to German patents 299074 (1916) and 369502 (1913) issued to Oscar Matter, the Th. Goldschmidt A.-G. produced considerable amounts of glycol during the World War.

99 parts ethylene chloride (1 molecule) require for saponification
106 parts sodium carbonate (1 molecule) or
168 parts sodium bicarbonate (2 molecules) and give theoretically
62 parts glycol.

To produce 100 parts of glycol theoretically 159.7 parts of ethylene chloride are required. The weaker the carbonate solution and the weaker its alkalinity the more the reaction goes toward the formation of glycol and the better the yields. An amount of water 15 to 20 times that of the ethylene chloride has been found best. For the same reasons the weaker bicarbonate alkali gives better yields, but has the economic disadvantage that two molecules, or a considerably larger quantity of a more expensive reagent, are required, and two molecules of carbon dioxide are produced, increasing the autoclave pressure.

Lead oxide, cadmium hydroxide and calcium carbonate have proved to be good saponifying agents, lead oxide having the advantage of allowing the glycol solution to be easily separated from the insoluble lead chloride and lead oxychloride. Zinc oxide and magnesia are unsuitable because the corresponding chlorides hydrolyze easily, and their solutions act chemically upon the glycol. The insoluble saponifying agents, in addition to the advantage of low alkalinity, have the disadvantage of requiring agitation in the autoclave for prompt saponification, and the autoclaves are very difficult to keep tight at high pressures. Absolutely tight autoclaves are necessary to avoid loss of ethylene chloride.

Saponification of ethylene chloride to glycol is possible with large quantities of water alone, without any alkali, under pressure at corresponding temperatures. However, the acid set free reacts at the temperatures in question to form aldehyde ($\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}-\text{H}_2\text{O} = \text{CH}_3\text{CHO}$) and croton aldehyde ($2\text{CH}_2\cdot\text{CHO}-\text{H}_2\text{O} = \text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CHO}$) and affects the yields.

Glycol yields with different saponifying agents and without agitation

	per cent of theory
Lead oxide or hydroxide.....	65
Cadmium hydroxide	67
Magnesium hydroxide	30
Barium carbonate	57
Calcium carbonate.....	67
Potassium carbonate.....	71
Sodium carbonate	81
Sodium bicarbonate.....	86

On account of its somewhat higher alkalinity potassium carbonate acts somewhat less favorably than sodium carbonate.

According to Matter an amount of water 15 to 20 times the quantity of ethylene chloride is taken and the whole saponified in an autoclave at 130 to 140°C. High temperatures favor the reaction. Too high temperatures cause side reactions and formation of resins. Preferably only a part of the quantity of carbonate required for saponification is added at first, and the consumed carbonate replaced by sodium hydroxide as the carbonate is used up, the sodium hydrox-

TABLE 14
Saponification of ethyl chloride and alkali

	ETHYLENE CHLORIDE	WATER	ALKALI	EXCESS OF ALKALI	CONCENTRATION OF ALKALI
				per cent	
1	240 grams 2 × 120 grams	1,200 cc. 10 times	283 grams 2 × 141.5 grams Na ₂ CO ₃	10	10.6
2	150 grams 2 × 75 grams	1,500 cc. 20 times	280 grams 2 × 140 grams NaHCO ₃	10	8.5

	TEMPERATURE	TIME OF HEATING	MAXIMUM PRESSURE IN ATMOSPHERES	GLYCOL	PER CENT OF THEORY	CONCENTRATION OF GLYCOL SOLUTION
				grams		per cent
1	150	48 hours 2 × 24 hours	38.0	122.2	81.3	9
2	160	28 hours 4 × 7 hours	40.5 27.0 41.0 30.0	80.7	86.0	5

ide forming new carbonate with the carbon dioxide present and thus reducing the excessive pressures in the autoclave to more moderate pressures.

Since there was a scarcity of caustic alkali during the war the total quantity of soda was added at first and the carbonic acid exhausted from time to time in order to operate at moderate pressures. The unconverted ethylene dichloride blown out with the carbon dioxide was recovered in absorption towers.

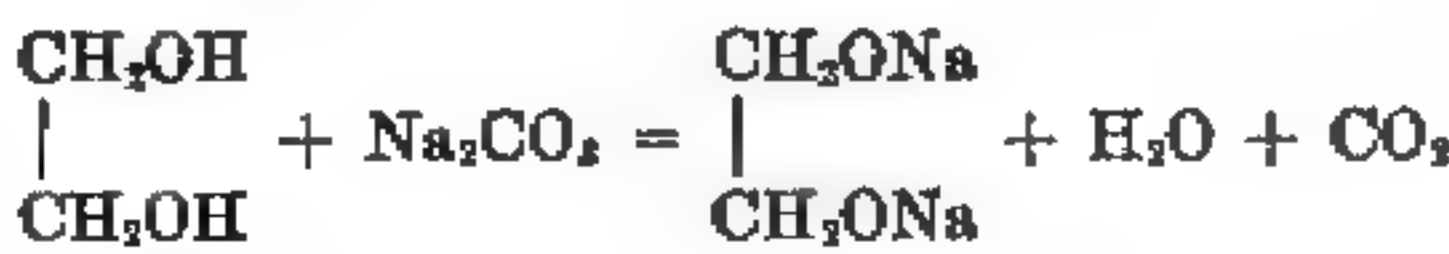
Examples of autoclave saponification in a 2-liter copper autoclave, placed in an oil bath. In order to obtain as high a strength of glycol solution as possible for further operations after the saponification a second amount of ethylene chloride and alkali were added to the common salt-glycol solutions and the saponification carried out in two stages. When using the bicarbonate the carbon dioxide was occasionally released when 40 atmospheres was reached, and the heating then continued. (See table 14.)

(d) Recovery of the glycol. The working up of the sodium chloride-glycol solutions obtained is similar to that of the recovery of distilled glycerine from soap lye, the only difference being that very little impurities are encountered if too high saponification temperatures and too high alkali concentrations are avoided. The concentration is done in a vacuum in the same apparatus as that in which soap lyes are concentrated. Ordinary pressures are out of the question because in such a case considerable glycol would be lost with the steam.

The salt is separated in stages, drained or centrifuged and covered with water to wash out any retained glycol, and the washings returned to the concentration.

After removal of the main quantity of salt the concentrated glycol, still containing salt, is distilled in a vacuum. It passes over at 110°C. in a high vacuum.

If an excess of alkali carbonate is used it must be exactly neutralized before the final distillation, because at the temperature of distillation it forms glycolates, which retain a part of the glycol in the still.



The loss of glycol in the concentration and salt separation does not amount to more than 2 per cent of the total quantity present, with careful operation. It can be determined exactly by extracting from the separated salt by methyl alcohol.¹⁴

Properties of glycol

Glycol is a colorless, very sweet tasting, somewhat syrupy liquid having a specific gravity of 1.1160 at 15°C. (with water at 4°C.). It

¹⁴ United States patent 1402317 (1922), saponification by soda in 85 per cent alcohol with sodium acetate as catalyst at 125 to 175°C. under pressure.

is more viscous than water but considerably less so than glycerine. The time taken for 5 cc. to run out of a 10 cc. pipette at 20°C. is:

	<i>seconds</i>
Water.....	4.5
Glycol.....	12.5
Monochlorohydrine.....	100.0
Glycerine.....	780.0

Under ordinary pressure it boils without decomposition at 194°C. (197.5°-E. E. R), in the vacuum of a water jet pump at about 110°C., and is somewhat volatile at ordinary temperatures. The presence of small quantities of water reduces the boiling point appreciably and considerable quantities of glycol pass over with the water vapor until a constant boiling point is reached. It crystallizes on strong cooling, and melts at -11.5°C.

Glycol is difficultly soluble in ether but mixes in all proportions with methyl alcohol, alcohol and water, and like glycerine it is hygroscopic. In moist air it absorbs up to 60 per cent of water.

It dissolves calcium hydroxide and caustic alkalies very easily, forming glycolates.

Tests on glycol

The explosive plants require a purity of at least 97 per cent glycol. The glycol content can be determined by oxidation with bichromate, like glycerine. Since the distillate obtained is usually very pure and contains no appreciable quantities of impurities other than water, a determination of the specific gravity is usually sufficient to determine its purity. For glycol contents between 90 and 100 per cent the following table of specific gravities at 25°C., with water at 4°C., can be used:

1.1023 specific gravity at 25°C.	= 90 per cent glycol
1.1030 specific gravity at 25°C.	= 91 per cent glycol
1.1038 specific gravity at 25°C.	= 92 per cent glycol
1.1045 specific gravity at 25°C.	= 93 per cent glycol
1.1052 specific gravity at 25°C.	= 94 per cent glycol
1.1060 specific gravity at 25°C.	= 95 per cent glycol
1.1067 specific gravity at 25°C.	= 96 per cent glycol
1.1074 specific gravity at 25°C.	= 97 per cent glycol
1.1081 specific gravity at 25°C.	= 98 per cent glycol
1.1089 specific gravity at 25°C.	= 99 per cent glycol
1.1096 specific gravity at 25°C.	= 100 per cent glycol

In other respects glycol is tested in about the same way as dynamite glycerine.

Direct determination of water in pure glycol. On account of the high volatility of the glycol the water cannot be determined as simply as in the case of glycerine. Heating is not permissible. Even in a desiccator the water is given up only slowly, even to a strong dehydrating agent like P_2O_5 . The determination is made as follows: The aqueous glycol is subjected to distillation, the boiling point rising gradually until it reaches a constant and anhydrous glycol passes over. The preliminary distillate contains all the water, for example 10 per cent of the total quantity, is placed in a thin layer in a desiccator over P_2O_5 and weighed daily until the loss of weight becomes constant. The loss of weight then corresponds to the quantity of glycol evaporated per day. The total reduction, diminished by the product of the number of days and the quantity of glycol lost per day, gives the quantity of water contained in the originally distilled total glycol. The determination is exact, but on account of the time taken is only used for special purposes and not for control.

Test nitration. A test nitration is used to judge the suitability of glycol intended for nitration. This is carried out in exactly the same manner, with the same apparatus and with the same mixed acids as in the test nitration of glycerine. One hundred grams of anhydrous glycol with 625 grams of mixed acid (40 per cent HNO_3 , 60 per cent H_2SO_4) at 10 to 12°C. as the temperature of nitration, yield 222 grams, at 29 to 30°C. temperature of nitration 218 grams of neutral dry nitroglycol, or with 500 grams of a mixed acid containing 50 per cent HNO_3 , 50 per cent H_2SO_4 at 10 to 12°C. the yield is 229 per cent dry nitroglycol from anhydrous glycol.

Manufacture of nitroglycol. The most favorable nitrating conditions for glycol are the same as for nitroglycerine, as would be expected from the close chemical relationship and very similar stoichiometrical relations of both alcohols.

100 parts glycol require for nitration 203.2 parts HNO_3

100 parts glycerine require for nitration 205.4 parts HNO_3

100 parts glycol give 245.2 parts nitroglycol and 58.1 of H_2O

100 parts glycerine give 246.7 parts nitroglycerine and 58.7 of H_2O

The commercial manufacture of nitroglycol is carried out in the same plant and with the same apparatus as nitroglycerine. Moreover, the composition and quantities of the mixed acid can be the same. The same can be said of the separation and washing, so that there is hardly anything in particular to be said regarding the manufacture of nitroglycol.

The quantity of heat set free in the nitration of glycol is slightly higher than in the nitration of glycerine, according to experimental determinations made by the Zentralstelle für wissenschaftlich-technische Untersuchungen, Neubabelsberg, a difference which is of no importance in practice. The lower viscosity of the glycol makes any preheating of it superfluous, and the low freezing point permits of maintaining lower nitrating temperatures, for example by artificially cooled brine, without fear of crystallization in the nitrator, which has a favorable effect upon the yields. In washing it is best not to use too high temperatures or too long periods of washing with compressed air, on account of the volatility of the glycol. Avoidance of too large amounts of wash water is even more important than in the case of nitroglycerine, since nitroglycol is appreciably more soluble in water. The solubility in spent acids is about the same as nitroglycerine.

Yields. The maximum yields obtained from 100 kg. anhydrous glycol and 625 kg. of mixed acid containing 58 per cent H_2SO_4 , 41 per cent HNO_3 and 1 per cent H_2O to 100 kg. of glycol were:

222.2 kg. nitroglycol, Nitrating at 10 to 12°C., or
218.3 kg. nitroglycol, Nitrating at 29 to 30°C.,

or in the best case 90.6 per cent of theory, as compared to 93.6 per cent with nitroglycerine. With 500 kg. of mixed acid containing 50 per cent HNO_3 and 50 per cent H_2SO_4 100 kg. glycol give 229 kg. nitroglycol (93.4 per cent of theory).

Tendency toward decomposition. The tendency of acid nitroglycol to decompose, with spontaneous saponification and evolution of nitrous acid, is less than with nitroglycerine under the same conditions. The following comparative tests show this. A charge of 100 grams of nitroglycol was left in a separatory funnel loosely covered with a glass plate for seventy-two hours in a cool place. Nitroglycerine was treated similarly. The quantities and compositions of the mixed acids, and the temperatures of nitration had been the same in both cases. After one day the oils became dark yellow and the separator above them filled with yellow vapors. After three days the nitroglycerine became green, a sign that considerable quantities of nitrous acid had formed, and the red vapor evolved was appreciably more than in the case of the nitroglycol. On neutralization of the oils there remained 204 grams of nitroglycol (218 grams was obtained before such treatment) and only 150 grams of nitroglycerine (225

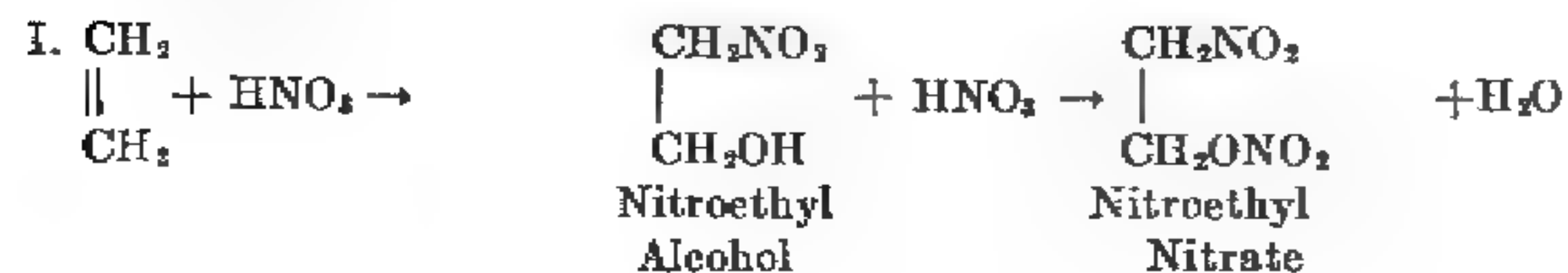
grams before treatment), and on washing considerable slime was formed. Thus under the same conditions only 14 grams of nitroglycol as compared to 75 grams of nitroglycerine had decomposed.

A certain parallel is also afforded by the fact that neutral nitroglycol also shows a higher stability on long heating than does neutral nitroglycerine.

Direct production of nitroglycol from ethylene. In recent times patents by the Chemische Fabrik Kalk, G. m. b. H., in Köln-Kalk, and Dr. H. Oehme, have described a process of preparing nitroglycol by the direct action of mixed acid on gaseous ethylene. Even Kekulé¹⁵ obtained an oil having a specific gravity of 1.47 by passing ethylene into a mixture of concentrated nitric acid and sulphuric acid, which on distillation in a current of steam broke down into glycollic acid, oxalic acid, NO and HNO₃ for the greater part, but he did not explain the chemical nature of the product. Since on reduction with caustic alkali solutions and sodium amalgam glycol and ammonia were formed among other things, it was suspected that it consisted in part of nitroglycol.

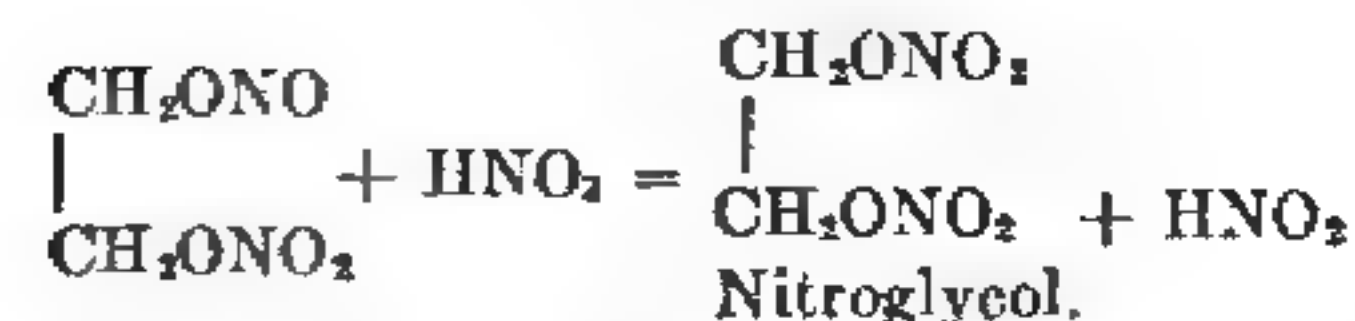
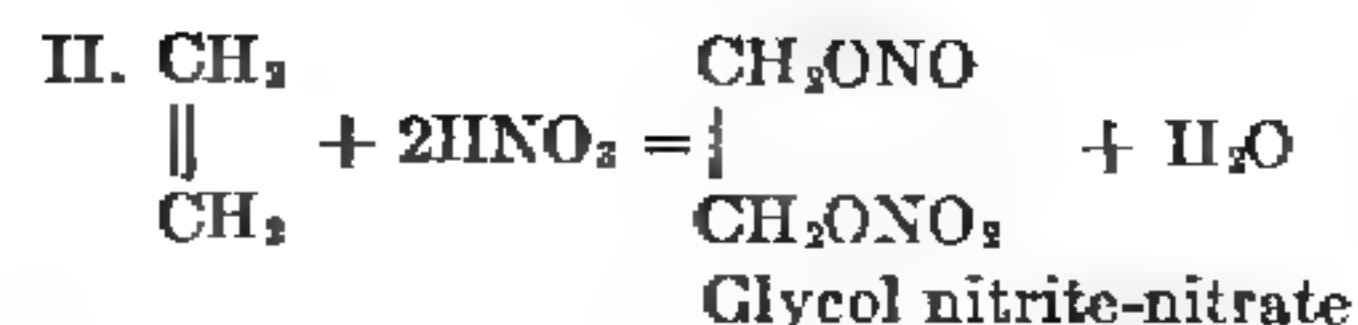
Wieland and Sakellarios¹⁶ first distilled the oil with steam and then fractionated in a vacuum, obtaining nitroglycol and β -nitroethyl nitrate. The nitroglycol passed over at 105°C. under 19 mm. pressure, the nitroethyl nitrate at 120 to 122°C., under 17 mm. Nitroethyl nitrate was also obtained by the direct action of mixed acid on β -nitroethyl alcohol. It has a weak acid character, and dissolves in cold caustic alkali solutions, giving a yellow color. If the Kekulé oil is distilled slowly in a current of steam a product is obtained consisting of about 80 per cent nitroglycol, from which the nitroethyl nitrate can be removed by shaking with very dilute caustic alkali, leaving pure nitroglycol.

The action of mixed acid on ethylene can be represented as follows:



¹⁵ Ber., 2, p. 329.

¹⁶ Ber. (1920), p. 201.



Both reactions take place simultaneously. The second, in which the glycol nitrite-nitrate is formed and in which a third molecule of nitric acid drives out nitrous acid, explains the rather high content of nitrous acid in the spent acid.

The crude Kekulé oil, when freed from admixed and dissolved acid by washing with water, contains about 40 to 50 per cent nitroglycol and 40 to 50 per cent nitroethyl nitrate.

Nitroglycol contains 18.42 per cent nitrogen, which is split off completely in the nitrometer as NO. Nitroethyl nitrate contains 20.59 per cent nitrogen, of which 10.29 per cent is split off in the nitrometer as primary nitrogen. The Kekulé oil on analysis gives 19.5 to 19.17 per cent total nitrogen and 13.5 to 14.3 per cent primary nitrogen.

As would be expected from its composition this mixture is a highly brisant explosive, equalling nitroglycerine and nitroglycol in explosive strength. It is formed in considerable quantities when a current of dry ethylene is passed through a concentrated mixture of nitric and sulphuric acids, the latter being constantly shaken or mechanically stirred. According to German patent 310789 (1918) a mixed acid containing about 32 per cent HNO₃ is used. The yield amounts to 350 per cent of the gas absorbed (theoretically 543 per cent for nitroglycol, 486 per cent for nitroethyl nitrate) composed of 40 per cent nitroglycol and 60 per cent nitroethyl nitrate, or about 70 per cent of the theoretical yield.

According to the same patent the washed oil is converted into a powder by taking it up in absorbents like kieselguhr or gelatinized with nitrocotton to form gelatinous explosives, just like nitroglycerine.

Direct separation of the oil from the spent acids accounts for only two-thirds of the total oil. The spent acids still contain about 8 to 10 per cent of their weight in solution, which according to German patents 349349 and 360455 can be largely separated by adding ammonia salts such as ammonium sulphate or nitrate, or after a certain

dilution, by sodium salts such as sodium sulphate, bisulphate or nitrate. The oil can be completely separated from the spent acids only by the aid of organic solvents like chloroform or ethylene chloride.

The oil when merely separated from the mineral acids does not have a sufficient stability for use in commercial explosives. The nitroethyl nitrate has a weak acid character, and under the action of gentle heat suffers a gradual decomposition or saponification, splitting off nitrous acid, and under certain conditions undergoing violent fuming.

A simple method of formation of nitroglycol from the crude product of the treatment of ethylene by mixed acids is described in German patent application C. 29462 (July 7, 1920) published May 31, 1923.¹⁷ Here the crude oil is treated with steam, i.e., slowly distilled with steam or better digested with water at 80 to 90°C. until the nitrocompounds it contains are almost completely converted into products soluble in water. The undissolved portion is separated, neutralized, and consists of almost pure nitroglycol. From 100 parts of crude oil about 40 parts of nitroglycol are obtained. The so-called acid waste waters contain, in addition to nitric acid, organic acids as valuable by-products.

According to application C. 31535, December 27, 1921, published July 23, 1923,¹⁸ the neutralization of the crude oil after treatment with hot water is done by neutral sodium sulphite, in order to avoid the formation of emulsions which occur when strong alkalis are used. If necessary a further stabilizing treatment is given with alkalis after the sulphite treatment.

The economy of the process depends upon a cheap source of ethylene,¹⁹ and upon the possibility of recovering valuable by-products from the destroyed nitroethyl nitrate.

Nitration of ethylene oxide. According to German patent 376000, (1920) ethylene oxide is passed into concentrated nitric acid, and after saturating the latter with the gas sulphuric acid is added, separating out an oil containing at least 16 per cent nitrogen by nitrometer determination and consisting mainly of glycol dinitrate and polymerization products of nitrated ethylene oxide.

¹⁷ German patent 384107.

¹⁸ German patent 386687.

¹⁹ German patent 369368.

According to German patent 377268 (1920) this oil is stabilized by treatment with steam or hot water.

The ethylene oxide is obtained from chlorohydrine, which is prepared by treating ethylene with solutions of hypochlorous acid. Nothing is known regarding the economy and yields with this process.

Properties of nitroglycol. Nitroglycol is a water-white, slightly syrupy liquid, having a specific gravity of 1.496 at 15°C. It is therefore somewhat lighter than nitroglycerine, which is 1.60. The viscosity is considerably less than that of nitroglycerine. The time taken for 5 cc. to run out of a 10 cc. pipette at 20°C. is:

Water	4.5 seconds (100)
Nitroglycol.....	5.0 seconds (111)
Nitroglycerine.....	12.5 seconds (278)

The freezing point has not yet been determined. It cannot be crystallized by immersing in a mixture of ice and salt, not even when mixed with kieselguhr. Nitroglycol explosives do not freeze at ordinary winter temperatures.

Nitroglycol cannot be distilled at ordinary pressures without decomposition, but it is easily volatile in a current of steam, more so than nitroglycerine. In the vacuum of a water jet pump it boils at about 95°C. without decomposition.

Volatility. Nitroglycol is appreciably volatile even at ordinary temperatures, and considerably so at a gentle heat. The loss in weight of about 15 grams in an open glass dish 65 mm. diameter and 40 mm. high was:

1. At 20°C. after 24 hours, 0.14 per cent; after 12 days,	2.06 per cent
At 20°C. after 48 hours, 0.37 per cent; after 30 days,	6.91 per cent
At 20°C. after 1 week, 1.63 per cent; after 6 months,	47.0 per cent
At 35°C. after 24 hours, 3.6 per cent; after 12 days,	46.6 per cent
At 35°C. after 48 hours, 8.1 per cent; after 20 days,	68.5 per cent
At 35°C. after 1 week, 21.7 per cent; after 40 days,	100.0 per cent

From a powdery explosive containing 5 per cent liquid nitroglycol, stored in an open dish in a thin layer at room temperature, more than one-half of the nitroglycol present had evaporated in twelve days, and almost all of it in five weeks. This was due to the large surface exposed. From a cartridge of the same explosive lying in the open, in waxed paper shells, only 2 per cent evaporated in twelve days, and only 12 per cent in two months. After 6 months only about one-half was left.

At 30 to 35°C. about 30 per cent of the nitroglycol had evaporated in 12 days, in four weeks about one-half, from filled cartridges. On the other hand, when the cartridges were packed in the ordinary way in a tight box only 10 per cent had evaporated after two months at room temperatures.

When the box was stored at 36°C., 14 per cent of the nitroglycol had evaporated after two months, and 40 per cent after six months.

Hygroscopicity. Nitroglycol has no more greater hygroscopicity than nitroglycerine.

Solubility. Nitroglycol is readily soluble in alcohol, ether, chloroform, acetone, benzene, toluene and nitrobenzene, but on the other hand only slightly soluble in carbon tetrachloride and benzine. The solubility relations of nitroglycol are not essentially different from those of nitroglycerine, aside from its solubility in water. The solubility in water is:

At 15°C. 1 liter of water dissolves 6.2 grams nitroglycol

At 20°C. 1 liter of water dissolves 6.8 grams nitroglycol

At 50°C. 1 liter of water dissolves 9.2 grams nitroglycol

At 20°C. 1 liter of water dissolves 1.8 grams nitroglycerine

The solubility in water is therefore appreciable and must be taken into consideration in all operations.

Gelatinizing powers. Nitroglycol gelatinizes nitrocotton much faster than does nitroglycerine. Gelatinization takes place in a short time even at ordinary temperatures, while with nitroglycerine heat must be used.

Chemical properties. On heating with free alkalis nitroglycol is saponified, like nitroglycerine. With alcoholic potassium hydroxide it reacts violently and forms potassium nitrate and glycolate.

Physiological properties. Nitroglycol causes headache, just like nitroglycerine. On account of its volatility its effects on the workmen are more violent than those of nitroglycerine. For this reason heat should be avoided, and good ventilation provided.

Chemical tests. Just as with nitroglycerine, the tests for purity are made with the Lunge nitrometer and expressed as per cent of nitrogen, which should be 18.42 per cent.

It can be distilled in a vacuum on an oil bath without danger.

Explosive character. Nitroglycol, with its ideal decomposition equation, which is a smooth breakdown into carbon dioxide, water and nitrogen, $\text{CH}_2\text{ONO}_2 \cdot \text{CH}_2\text{ONO}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2$, is the

most powerful of all the chemically homogeneous explosives which have found practical use up to the present time, and in energy content it exceeds even nitroglycerine. Among the nitric esters it, together with nitroisobutylglycerine trinitrate, occupies first place. The corresponding chloric and perchloric esters contain even more energy on account of the lower heat of formation of these acids in similar decomposition equations, but they are either very difficult to make or are unstable in the presence of moisture, like the perchloric ester, so that they have found no practical application up to the present time. In addition to this they are dangerous to handle. On the other hand, the highly nitrated aromatic nitrocompounds, which approach the energy content of these nitric esters very closely, like tetranitroaniline, tetranitrophenylmethylnitramine and pentanitrophenylmethyl nitramine,²⁰ are chemically unstable.

Of the highly stable, easily prepared and relatively safe explosives, nitroglycol occupies first place as regards strength. On explosion 1 kg. of it develops:

1705.3 Calories at constant volume and water Liquid, or
1580.9 Calories at constant volume and water Gaseous.

The molecular heat of formation is 67.7 Calories. Therefore nitroglycol has a total energy content exceeding that of nitroglycerine (1595 Calories H_2O liquid) by 6.9 per cent.

Just as with nitroglycerine, the explosive decomposition can be started by sudden heating, shock or initiation. On rapid heating nitroglycol explodes at about 215°C. with a sharp report.

Sensitiveness to shock. Under the falling weight nitroglycol, both as such and in the form of a dynamite, has a considerably lower sensitiveness than nitroglycerine. Under the 2 kg. weight in comparative tests with nitroglycerine²¹ the latter gave 8 to 10 cm., the former 20 to 25 cm. for detonation, nitroglycerine blasting gelatine 12 cm., nitroglycol blasting gelatine 25 to 30 cm., nitroglycerine guhr dynamite 5 cm., nitroglycol guhr dynamite 15 cm.

Flammability. Both nitroglycol and explosives containing it ignite when in contact with a flame, and burn with sputtering unless a sudden overheating occurs, in which case there is an explosion,

²⁰ Stettbacher, *Schiess- und Sprengstoffe*, pp. 201-203.

²¹ A drop absorbed in filter paper.

just as with nitroglycerine. In general nitroglycol explosives burn more quietly than do those containing nitroglycerine, and have less tendency to explode than the latter.

Chemical stability. In the Abel test at 72°C. nitroglycol gives a reaction quickly. However, this should be attributed to the relatively high evaporation and slight dissociation of the vapors, and in no case does it represent a low chemical stability. On long continued heating in a loosely covered weighing glass at 75°C. nitroglycol shows a considerably greater stability than does nitroglycerine, and only begins to decompose appreciably after eleven days (see under Nitroglycerine, page 135).

Sensitiveness to initiation. Nitroglycol is very sensitive to initial impulse, and like nitroglycerine is exploded both in a liquid condition and as a dynamite by the weakest common cap, a No. 1, even without confinement. Small quantities when loosely confined, such as 10 grams in a lead block with water tamping, show a higher sensitiveness than nitroglycerine. This is true, however, only for the liquid condition. Correspondingly, nitroglycol explosives show a favorable propagation of detonation. Therefore nitroglycol, like nitroglycerine, is a suitable material to add in small quantities to ensure the propagation of detonation of explosives containing ammonium nitrate, chlorate or perchlorate, and to raise their velocity of detonation.

Velocity of detonation. The velocity of detonation of nitroglycol in a liquid condition does not appear to have as yet been measured. It should somewhat exceed that of nitroglycerine, but in any case it can be assumed to have a high value on account of the better propagation of the wave of detonation in liquids of low viscosity, even when in small tubes. With a 75 per cent kieselguhr mixture in tubes 35 mm. internal diameter, and a density of loading of 1.25 the author found:

	meters per second
With nitroglycol.....	6000
With nitroglycerine.....	5650

or 350 meters per second greater for nitroglycol.

Explosive strength. As regards energy content and high velocity of detonation nitroglycol occupies first place by the customary methods of determining explosive strength. The lead block expansion of 10 grams with water tamping was:

	Energy content
Nitroglycol, 650 cc. (110).....	107
Nitroglycerine, 590 cc. (100).....	100

In the ordinary explosive mixtures nitroglycol acts about the same as nitroglycerine. As regards explosive effect it is, therefore, a completely satisfactory substitute for the latter.

GLYCOL MONONITRATE



The mononitric ester of glycol is formed as a by-product in the manufacture of dinitroglycol, just as are mono- and dinitroglycerine in the manufacture of nitroglycerine. Chemically it is very similar to the lower glycerine nitrates.

According to Henry²² it is obtained by the action of silver nitrate on bromohydrine. It can also be formed directly from glycol by the same process as is used for dinitroglycerine:

One hundred grams of glycol is dissolved in 100 grams of nitric acid of a specific gravity of 1.515 (99 per cent HNO₃) with good cooling, and then 220 grams more of the same nitric acid added and this solution allowed to stand at 0°C. for one hour. The nitric acid should be as free as possible of nitrous acid, because otherwise there can be a violent oxidation and fuming-off of the entire charge. This solution is then poured on to ice, neutralized by soda and the small quantities of mono- and dinitrate separated. The salt-peter solution obtained is extracted several times with ether, and after removal of the ether the residue is fractionated in a vacuum. From the oil directly separated, the mononitrate is extracted by shaking several times with water and the solution fractionated in a vacuum. The product so obtained is still somewhat contaminated with nitroglycol, from which it is separated by dissolving in water. After driving off the water in a vacuum, it is again rectified. The theoretical yield is 172.6 parts from 100 parts glycol.

Direct separation from 100 grams of glycol gave about 58 grams of an ester mixture having a specific gravity of 1.40, consisting of about one-half dinitrate and one-half mononitrate. On a triple treatment with small quantities of water there finally remained about 30 grams of pure dinitrate. The aqueous extract, together with the neutralization liquors, gave 90 grams of mononitrate when extracted with ether, or a total of 120 grams of the esters.

30 grams dinitrate (25 per cent) correspond to 12.4 per cent of theory
90 grams mononitrate (75 per cent) correspond to 52.3 per cent of theory
Total glycol accounted for in ester 64.7 per cent.

²² *Ann. chim. et de physique* (4), 27, p. 243.

By using 400 grams of the same nitric acid and 100 grams of glycol, with a two-hour after-nitration at 0°C., mostly dinitrate was formed. On direct separation there was obtained 176 grams of an ester mixture having a specific gravity of 1.47, containing 84 per cent dinitrate and 16 per cent mononitrate. The total mononitrate obtained was 46 grams, so that:

148 grams dinitrate (76 per cent) correspond to 60 per cent of theory

46 grams mononitrate (24 per cent) correspond to 26.6 per cent of theory

194 grams glycol in the form of esters or 86.6 per cent of theory

The relations in the manufacture of dinitroglycerine and nitroglycerine by concentrated nitric acid are quite similar.

Properties. Glycol mononitrate is a water-white liquid having a slightly aromatic odor and a specific gravity of 1.348 at 20°C. (d)₄²⁰. It is only slightly more viscous than nitroglycol. In the vacuum of a water jet pump it boils without decomposition at 91 to 92°C., and is somewhat volatile at ordinary temperatures. It dissolves very readily in alcohol, ether and chloroform, but on the other hand is miscible in all proportions with water, and therefore resembles glycerine mononitrate.

It forms a good gelatine with collodion nitrocotton even at ordinary temperatures. It is converted into nitroglycol by the action of concentrated nitric acid or mixed acid. It dissolves in concentrated sulphuric acid with a considerable evolution of heat, so that in the determination of the nitrogen content by the Lunge nitrometer it should be first dissolved in a moderately strong sulphuric acid and then the concentrated sulphuric acid added gradually. Its nitrogen content is theoretically 13.08 per cent.

Explosive character. Glycol mononitrate has an oxygen deficiency of 37.4 per cent, but is nevertheless a powerful explosive. When heated rapidly, it explodes violently. In a lead block, 10 grams in a glass tube, with sand tamping, gave an expansion of 375 cc., while nitroglycol gives 650 cc. One kilogram on explosion develops 943.7 Calories at constant volume with water liquid, or 855.6 Calories at constant volume with water gaseous. The molecular heat of formation is 90.0 Calories. The ratio of energy content of glycol dinitrate to mononitrate is 100:54.1; the ratio of the lead block expansions is 100:57.7.

Glycol mononitrate has not been considered for commercial explosives because it has no advantages over the dinitrate, and moreover its manufacture is more difficult and its solubility in water is a serious disadvantage.

TRIMETHYLENE GLYCOL DINITRATE

*Trimethylene glycol and its nitric ester, trimethylene glycol dinitrate*

Formerly unknown, trimethylene glycol and its nitric ester achieved a certain importance during the World War, which caused a more extensive investigation of such bodies. Fermentation glycerine, or protol glycerine, obtained by the fermentation of sugar, which was used in the latter years of the war in Germany in large quantities for the manufacture of nitroglycerine, usually contains small amounts of trimethylene glycol, formed in considerable quantities under certain conditions or on further treatment of the wort.

Trimethylene glycol has been found occasionally in dynamite glycerine produced from fats, (soap spent lyes, glycerine waters), and Freund²³ has shown that under certain conditions glycerine is converted into trimethylene glycol by the action of certain bacteria,²⁴ for example if impure, dilute glycerine solutions are stored for a long period, as is frequently the case with glycerine sweet waters.

Trimethylene glycol is found in fermentation glycerine apparently in larger quantities than in glycerine produced from fats. Its formation is considered a disadvantage because it reduces the yield of dynamite glycerine from sugar considerably, and also seems to affect the nitration unfavorably if present in larger quantities.

A close study of the fermentation in protol plants has shown that normally fermented mash usually contains a very small amount of trimethylene glycol. The formation of the latter is due rather to the activity of micro-organisms such as yeasts and stray bacteria, which attack the glycerine after fermentation of the original sugar and so form the trimethylene glycol as a by-product. The higher the sulphite content of the protol wort or slop the less the subsequent fermentation of glycerine and formation of trimethylene glycol, and on the other hand the lower the sugar content of the wort the greater the danger of subsequent loss of glycerine. In concentrated slop the high salt content hinders this reaction, and it is also affected by the presence of alcohol and aldehyde, so that considerable trimethylene glycol is formed if the de-

²³ *Monatshfte, f. Chem.*, 11, p. 636 (1881).

²⁴ Perhaps identical with *Bacillus Butyricus*, isolated by Fitz, *Ber.* 9, p. 1348, or with the mould *Botrytis Cinerea*, which should also form trimethylene glycol, Laborde, *Rev. de Viticulture* (1897). See also Neuberg and Färber, *Biochem. Z.*, 78, 3, 4, p. 264 (1916).

alcoholized, dilute worts are allowed to stand for a long time before treatment. It is therefore best to treat them by driving off the alcohol and evaporating the wort as soon as possible after the fermentation is complete.

In the distillation of dynamite glycerine from the slops the greater part of the trimethylene glycol present then goes into the so-called sweet waters, on account of its lower boiling point, and after their concentration it can be easily separated from the glycerine by fractionation.

In addition to trimethylene glycol the preliminary run of protol glycerine contains a whole series of esters of various organic acids, and if they contaminate the glycerine there is likewise danger of undesirable side reactions in the nitration of the latter.

Properties of trimethylene glycol. Pure trimethylene glycol is readily obtained at good yields by saponification of 1,3-dibromopropane (trimethylene bromide, boiling point $165^{\circ}\text{C}.$) by potassium bicarbonate. Trimethylene bromide is boiled with a 10 to 15 per cent solution of KHCO_3 for about twelve hours under reflux until all the bromide has dissolved, the water removed by a vacuum, and the moist mixture of KBr and glycol extracted by a mixture of methyl alcohol and ether, and after removal of the latter, rectified. The yield is about 85 per cent of theory.

Pure trimethylene glycol is a colorless, odorless, syrupy, sweet liquid having a specific gravity of 1.0526 at $18^{\circ}\text{C}.$, boiling without decomposition at $211^{\circ}\text{C}.$, and mixing with water and alcohol in all proportions.

When isolated by repeated fractional distillation from protol glycerine, it is yellow, with a peculiar, slightly burnt odor resembling coffee, boiling at 209 to $210^{\circ}\text{C}.$, a specific gravity of 1.0536 at $18^{\circ}\text{C}.$ referred to water at $4^{\circ}\text{C}.$ It contains 0.6 to 0.7 per cent of sulphur. It dissolves lead acetate if heated, and on gentle heating for some time forms a brownish-black precipitate. On heating with litharge the latter turns black after some time.

Protol glycerine also contains 0.4 to 0.5 per cent sulphur. The nitroglycerine made from it contains about 0.3 per cent sulphur. The dinitrate from the isolated trimethyleneglycol contains about 0.2 per cent sulphur.

Determination of the trimethylene glycol content of protol glycerine. The trimethylene glycol content of a dynamite glycerine can be calculated from the specific gravity. With water present at the same time the determination of the specific gravity requires the use of the Rojahn Tables to show the trimethylene glycol content, for

which see *Z. f. analyt. Chem.*, 58, 433 (1919); "The Effect of the Presence of Trimethylene Glycol Upon the Quantitative Determination of Glycerine by the Isopropyl Iodide Method."²⁵

Manufacture of Trimethylene glycol dinitrate

Nitration of trimethylene glycol. This can be readily nitrated to the corresponding dinitrate by mixed acid, using certain precautions, such as maintenance of low temperatures. This so-called nitration, or rather esterification, takes place very smoothly, without any tendency toward oxidation in the case of methyl alcohol and those polyvalent alcohols containing one hydroxyl group on every carbon atom but no methyl- or methylene group, like glycol, glycerine, erythrite, pentaerythrite or mannite. The monovalent alcohols, with the exception of methyl alcohol, such as ethyl and propyl, are very violently oxidized by strong nitric acid or mixed acid, even at relatively low temperatures, so that their nitric esters must be prepared with comparatively weak nitric acid (specific gravity 1.4) with comparatively low yields.

The conditions are similar with the polyvalent alcohols like trimethylene glycol, propylene glycol and butylene glycol, whose smooth esterification by mixed acid at good yields is possible only at low temperatures.

The study of these nitrating conditions was therefore of importance because under certain conditions dynamite glycerine can contain some trimethylene glycol, as was often the case with protol glycerine made during the war in Germany. On account of the tendency of the trimethylene glycol to undergo violent oxidation fear was expressed regarding the safety of the nitroglycerine operations.

Trimethylene glycol requires only 166 parts of HNO_3 per 100 parts to convert it into the dinitrate, while glycerine requires 205.4 parts for the trinitrate. Five hundred parts of mixed acid containing 40 per cent HNO_3 and 60 per cent H_2SO_4 are therefore sufficient for 100 parts of trimethylene glycol.

Temperature. On cooling by a mixture of ice and salt, and slow introduction of trimethylene glycol into the mixed acid, the nitration is perfectly smooth at 0 to $10^{\circ}\text{C}.$ Above $15^{\circ}\text{C}.$, and particularly above $20^{\circ}\text{C}.$, there is a tendency toward decomposition while adding

²⁵ See also *Ber.*, 52, 8, 1454.

the trimethylene glycol, yellow vapors being evolved with a hissing sound. In the second half of the nitration, when the acids were rather dilute, this oxidation tendency is less. If the trimethylene glycol is added too rapidly, so that the temperature rises to 30°C. a violent decomposition of the entire charge may occur, with a copious evolution of red fumes and even a firing.

The separation takes place smoothly at 10°C., and the separated oil is washed like nitroglycerine.

The phenomena observed by the author in the nitration or oxidation with impure natural trimethylene glycol obtained from protol glycerine, which usually contains traces of easily oxidized compounds or esters, are exactly the same as those observed with chemically pure trimethylene glycol obtained from saponification of pure trimethylene bromide, so that these properties must be peculiar to the chemical constitution.

Yields. From 100 grams of trimethylene glycol, prepared from protol glycerine, 198 grams of pure, neutral dinitrate were obtained. The theoretical yield is 218.4 grams so that the yield is 90.6 per cent of theory. Synthetic trimethylene glycol gives exactly the same yield as the above.

The nitrogen content by the Lunge nitrometer was:

	per cent
Trimethylene glycol dinitrate from protol glycerine.....	16.75
Trimethylene glycol dinitrate from synthetic product.....	16.83
Calculated.....	16.88

Properties of the spent acid. The behaviour of the spent acid from a trimethylene glycol nitration is peculiar. After some time a certain amount of spontaneous heating above room temperature to about 30°C. occurs. The trimethylene glycol dinitrate still dissolved, and other dissolved organic substances, undergo oxidation on standing which becomes evident by a gradual increase in the nitrous acid content of the spent acid. After storing for some time the acids are found to be saturated with carbon dioxide, and effervesce slightly on shaking.

After standing for a long time the spent acids from the nitration of synthetic trimethylene glycol show 9.0 per cent of NO₂, and 8.5 per cent when using a trimethylene glycol derived from protol glycerine. Similar nitroglycerine spent acids of the same age contain only 1.8 per cent of NO₂.

The spent acids contain about 2 per cent of dissolved dinitrate, which can be recovered by extraction with chloroform. This raises the yield to 205.3 per cent of the glycol, or 94 per cent of theory. Even the extracted spent acids show the peculiar subsequent oxidation, although to a less extent.

The nitrous acid content of the spent acid was as shown in table 15.

Even after the second day the temperature of the acid remained 4°C. above room temperature for several hours in the case of small laboratory charges of

TABLE 15
Nitrous acid content of spent acid

	I TRIMETHYLENE GLYCOL DINITRATE SPENT ACID	II SAME, AFTER EXTRACTION BY CHCl ₃
	per cent	per cent
Directly after nitration.....	1.6	2.7
After twenty-four hours.....	6.6	5.4
After two days.....	8.6	5.5
After three days.....	8.8	5.6
After seven days.....	9.2	5.8

TABLE 16
Oxidation during nitration of glycerine and trimethylene glycol

NO ₂ CONTENT	SPENT ACID I, 10 PER CENT TRI- METHYLENE GLYCOL		SPENT ACID II, 20 PER CENT TRI- METHYLENE GLYCOL	
		Increase per day		Increase per day
	per cent	per cent	per cent	per cent
Directly after separation.....	1.67		1.70	
After twenty-four hours.....	1.88	0.21	2.08	0.38
After three days.....	2.29	0.20	3.02	0.47
After five days.....	2.51	0.11	3.52	0.25
After eight days.....	2.74	0.08	3.92	0.13

0.5 to 1.0 kg. If the loss of heat by conduction in the case of small charges is taken into consideration it is evident that on a commercial scale large charges would have to be cooled for a long period.

Nitration of mixtures of glycerine and trimethylene glycol. Mixtures of glycerine and trimethylene glycol containing 5 and 10 per cent of the latter nitrate smoothly even at 30°C. without any sign of oxidation. The yields of the esters are lower than with glycerine alone and correspond to the trimethylene glycol content. With a mixture of 80 per cent glycerine and 20 per cent trimethylene glycol there was a slight tendency toward oxidation at the beginning of nitration at 20°C. After this the nitration went smoothly at 25°C.

With a 90/10 mixture of glycerine and trimethylene glycol the spent acids directly after nitration showed 1.67 per cent NO_2 , and with an 80/20 mixture 1.70 per cent NO_2 . Since a certain amount of oxidation accompanies every nitration, and even nitroglycerine spent acids contain 1.7 to 1.8 per cent NO_2 , these figures show that in the nitration of mixtures of glycerine and 10 to 20 per cent trimethylene glycol there is no marked oxidation during nitration. On storing the spent acids, however, there is a considerable oxidation, as is shown in table 16. Thus the reaction gradually dies out in the course of a week becoming rather small and corresponding to the actual quantity of trimethylene glycol present. No formation of CO_2 was noticed in spent acid I, but No. II showed some after a few days, particularly on shaking, although slight.

Accordingly glycerine containing less trimethylene glycol than the above should be no source of danger in nitration and other processes of nitroglycerine manufacture.

From the sweet water concentrate of a protol glycerine plant the author isolated by fractional distillation 25 per cent trimethylene glycol and 2 per cent of low boiling esters of organic acids, while the residue consisted of glycerine and water. When these very reactive esters, obtained as the preliminary fraction from trimethylene glycol, are put into mixed acid a small amount of an oily nitric ester separates, mainly trimethylene glycol dinitrate, but after some time the spent acids heat up spontaneously and undergo a violent decomposition.

Any "cut" of the protol glycerine containing such sweet water concentrates can therefore lead to surprising conditions in the nitroglycerine operations, due to lack of knowledge of these circumstances, as for example fires in after-separation during the war, which were traced to this cause.

Properties of trimethylene glycol dinitrate. Trimethylene glycol dinitrate is a water-white, very mobile, almost colorless liquid, with an extremely slight, ethereal-aromatic odor. It is considerably less viscous than nitroglycerine, and almost like nitroglycol in this respect. Its specific gravity at 20°C . is 1.393, referred to water at 4°C . It boils without decomposition under 10 mm. pressure at 108°C .

Volatility. It is considerably more volatile than nitroglycerine, but not so much so as nitroglycol. It is almost insoluble in water, but easily soluble in the same solvents as nitroglycerine, as well as in concentrated nitric acid, which causes a gradual decomposition, and in concentrated sulphuric acid with decomposition. It forms a

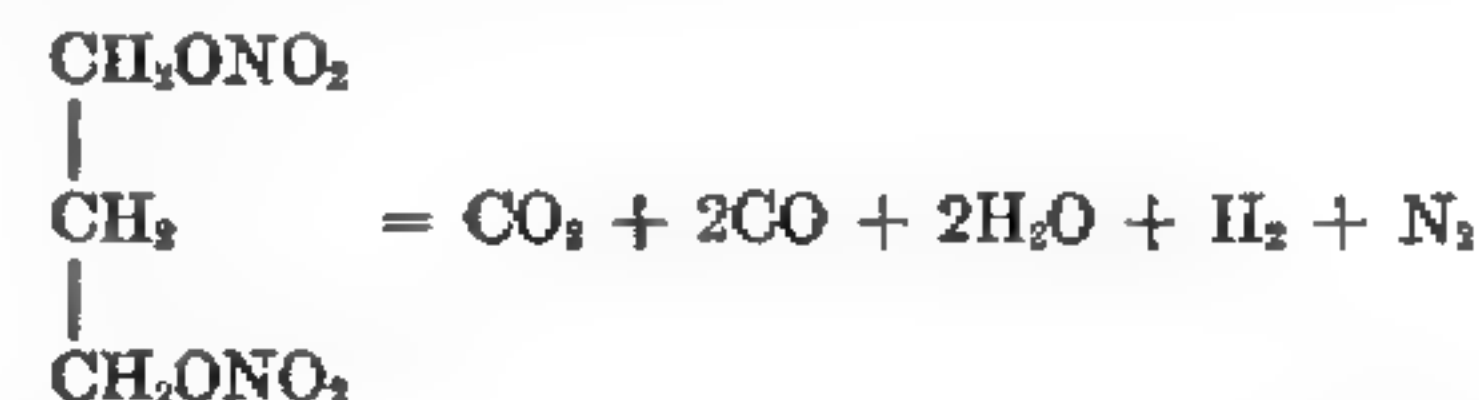
good gelatine with collodion nitrocotton. In contact with the skin it causes headache, like nitroglycerine.

On gradually heating small amounts of it in an iron dish it ignites with a slight report, after which the liquid burns quietly. On heating two drops in a beaker placed in a bath of molten metal yellow vapors were given off at 185°C ., which gradually became more voluminous. At 225°C . a slight deflagration occurred.

The sensitiveness to shock is very low. Under the 2 kg. weight it could not be detonated even at a 100 cm. drop, nor under the 10 kg. weight at a drop of 20 cm. Trimethylene glycol dinitrate is therefore much safer to handle than nitroglycerine.

Chemical stability. Although the Abel test reaction is obtained after only a few minutes, its chemical stability is extraordinarily high, even at higher temperatures. Small samples of trimethylene glycol dinitrate, stored in a loosely covered weighing bottle for twenty-five days at 75°C . showed no decomposition or development of acidity. The nitrogen content was the same after storage as before. There was merely a volatilization loss of about 5 per cent.

Explosive strength. Trimethylene glycol dinitrate lacks 28.9 per cent oxygen for complete combustion. For a decomposition according to the following equation:



with a molecular heat of formation of 78.1 Calories, there is a heat of explosion of 1138.5 Calories per kilogram at constant volume and water gaseous.

Trimethylene glycol dinitrate is therefore to be expected to be among the strongest highly brisant explosives. As a matter of fact, 10 grams of it in a lead block, with water tamping, gave an expansion of 540 cc., or about 90 per cent that of nitroglycerine, whereas the energy content can be calculated as only about 77 per cent of that of nitroglycerine. Here, as in other cases, like nitroglycide and dinitrochlorohydrine, the explanation lies in the ability of the liquid of low viscosity to give a high initial velocity of detonation.

A gelatine consisting of 93 per cent trimethylene glycol dinitrate

and 7 per cent collodion nitrocotton gave a lead block expansion of 470 cc., or about 80 per cent of the strength of a nitroglycerine gelatine.

PROPYLENE GLYCOL DINITRATE (METHYL GLYCOL DINITRATE)



This nitric ester, isomeric with trimethylene glycol dinitrate, and very similar to it, a high explosive, has been proposed as an addition to nitroglycerine to render the latter non-freezing, just like nitroglycol.²⁶ The high price and difficulty in obtaining the raw material, propylene glycol, has previously prevented its practical use, because more readily obtained products like dinitroglycerine, tetranitrodiglycerine, nitroglycol and dinitrochlorohydrine serve the same purpose.

Propylene glycol can be obtained by a synthesis analogous to that of the glycol synthesis from ethyl alcohol, from normal propyl alcohol or from the now readily obtainable isopropyl alcohol, today produced on a large scale by the catalytic reduction of acetone.²⁷ Isopropyl alcohol, when passed over Al_2O_3 at 300°C . gives propylene, and the latter by chlorination gives propylene chloride,²⁸ which on gentle saponification with carbonates or bicarbonates gives propylene glycol.

Propylene glycol is a thick, sweet-tasting liquid having a specific gravity of 1.04 at 20°C ., and boiling at 188°C . It is miscible in all proportions with water and alcohol.

Propylene glycol shows the same peculiar tendency toward oxidation during nitration as trimethylene glycol, but to a less extent, and can be easily converted into the dinitrate by 5 parts of a mixed acid containing 40 per cent HNO_3 and 60 per cent H_2SO_4 . Decomposition only occurs above 30°C .

Yields. From 100 parts the author obtained 187 parts of the dinitrate (theory 218.4), corresponding to about 86 per cent yield. The nitrogen content was 16.50 per cent, the calculated being 16.88 per cent.

Propylene glycol dinitrate is a water-white liquid having a charac-

²⁶ German patent 179789 (1904).

²⁷ And also from the gases from "cracking" petroleum.—TRANSLATOR.

²⁸ German patent 363269 (1919), Union Carbide Company, New York.

teristic, rather aromatic odor, which does not freeze at -20°C . It is two to three times as volatile as the isomeric trimethylene glycol dinitrate. It is somewhat less viscous than its isomer. Its specific gravity at 20°C ., with water at 4°C ., is 1.368. It boils at 92°C . under 10 mm. pressure. Its solubilities and gelatinizing powers are the same as the isomer. (See table 17.)

From a chemical point of view and as an explosive, propylene glycol dinitrate behaves like its isomer. With a molecular heat of formation of 83.1 Calories it has a heat of explosion of 1109 Calories per kilogram at constant volume with water gaseous, while the isomer evolves 1138.5 Calories. This slight difference predicts about the same explosive power, and as a matter of fact 10 grams of it under

TABLE 17

Loss of weight and viscosity of propylene glycol and trimethylene glycol

	PROPYLENE GLYCOL DINITRATE (10 GRAMS)	TRIMETHYLENE GLYCOL DINITRATE (10 GRAMS)
	per cent	per cent
Loss of weight at 35°C . in dishes 60 mm. in diameter:		
After twenty-four hours.....	3.8	1.8
After three days.....	14.1	4.2
	seconds	seconds
Viscosity, or time taken for 5 cc. to run out of a 10 cc. pipette at 20°C	5.0	5.5

water tamping give an expansion of the lead block of 540 cc., the same as trimethylene glycol dinitrate.

NITROERYTHRITE (ERYTHRITE TETRANITRATE)



The next higher homolog of nitroglycerine is erythrite tetranitrate. This is prepared from erythrite, which occurs in nature in algae and lichens, and has a melting point of 120°C ., a specific gravity of 1.59. It is very soluble in water. On adding it to highly concentrated nitric acid while cooling, then adding an equal quantity of concen-

trated sulphuric acid²⁹ the tetranitrate precipitates. It crystallizes in plates from alcohol and melts at 61°C. It is insoluble in cold water.

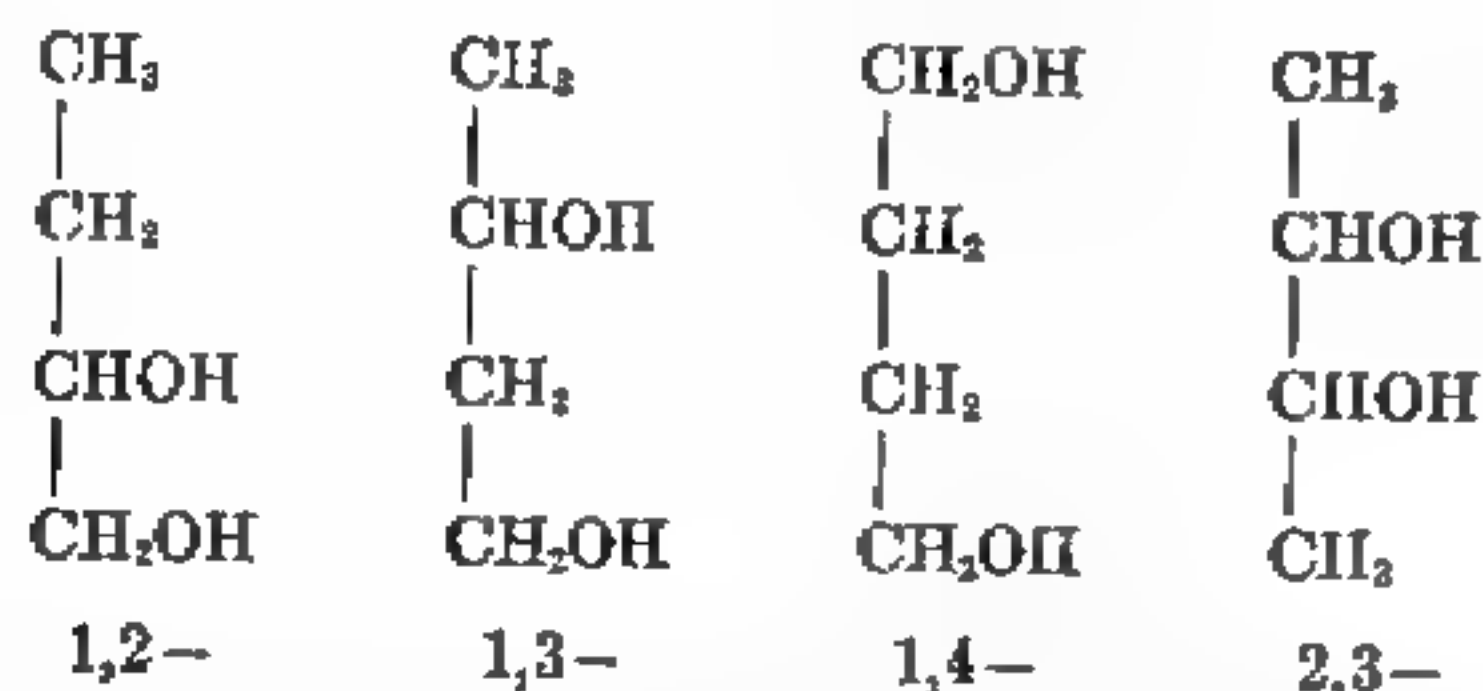
It is mentioned in German patent 110289 (1898) and English patent 27397 (1898) as an addition to smokeless powder. It detonates readily by shock, and on account of its favorable decomposition equation and an oxygen balance of +5.3 per cent, similar to that of nitroglycerine, it evolves an energy approximating that of nitroglycerine. With a molecular heat of formation of 130.5 Calories its heat of explosion is 1414 Calories per kilogram at constant volume and water gaseous.



Its lower chemical stability, and the difficulty in obtaining the raw material has prevented its practical use up to the present time, and may do so in the future.

BUTYLENE GLYCOL DINITRATE

Of the four following isomeric butylene glycols:



only the second, the 1,3-butylene glycol, has been proposed as a raw material for explosives and been tested. According to United States patents 994841 and 994842 (1911) its dinitrate, either alone or in admixture with nitroglycerine, is proposed as the basis of non-freezing explosives.

According to United States patent 1008333 (1911) the 1,3-butylene glycol is obtained from aldehyde via acetaldol by reduction of the latter, and then converted into the dinitrate in the usual way.

Although the synthesis of butylene glycol has made great progress in Germany in recent times, so that the product can now be supplied

²⁹ Stenhouse, *Liebig's Ann. d. Chem.*, 70, 226 (1849).

at a rather low price, it could not be introduced into the practical manufacture of explosives on account of too great difficulties in nitration, due to tendency toward oxidation, similar to certain glycols, trimethylene glycol in particular, which requires very good cooling and a very low temperature of nitration, at least -5°C .

According to the last mentioned patent the preparation of butylene glycol is as follows:

Butylene glycol is a thick, sweet-tasting liquid, less viscous than glycerine, having a specific gravity of 1.026, boiling at 203 to 204°C., or at about 110°C., in the vacuum of a water jet pump. It is very soluble in water and alcohol, and only slightly soluble in ether.

Nitration. On account of the tendency toward oxidation, nitration should be done at as low a temperature as possible, e.g., -5°C . An aqueous mixed acid helps the operation but reduces the yields. One hundred parts of butylene glycol give about 187.5 parts of the dinitrate (theory 200 parts), or 93.7 per cent of theory. The nitrogen content is 15.56 per cent.

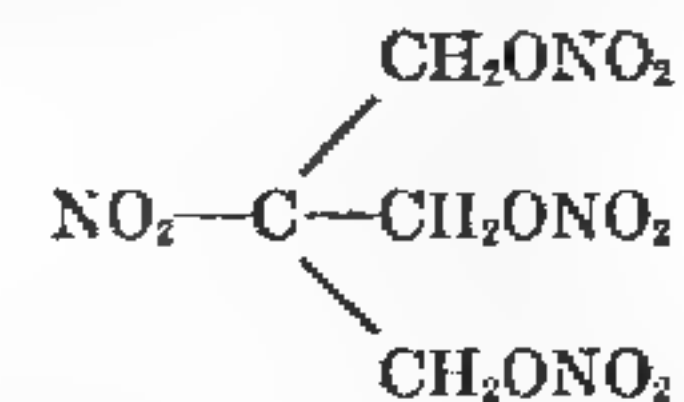
Properties of butylene glycol dinitrate. It is a water-white liquid having a specific gravity of 1.32 at 15°C., which does not freeze at -20°C . It is somewhat volatile even at ordinary temperatures, appreciably so at 50°C., considerably more so than nitroglycerine but less so than nitroglycol. It is insoluble in water but readily soluble in the same solvents as nitroglycerine.

Although it gives a reaction in the Abel Heat Test in a short time, it shows a high chemical stability at higher temperatures. It forms a good gelatine with collodion nitrocotton.

On sudden heating it deflagrates weakly. It is extraordinarily insensitive to shock but detonates easily by initiation.

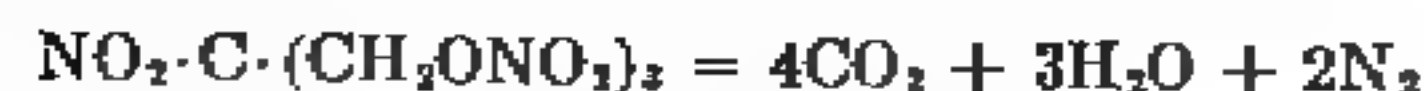
Explosive strength. A mixture of 75 per cent dinitrate and 25 per cent kieselguhr gives about 240 cc. expansion in the lead block. A gelatine containing 90 per cent dinitrate and 10 per cent nitrocotton gives about 370 cc. expansion. The oxygen balance of the dinitrate is -53.3 per cent.

NITROISOBUTYLGLYCERINE TRINITRATE



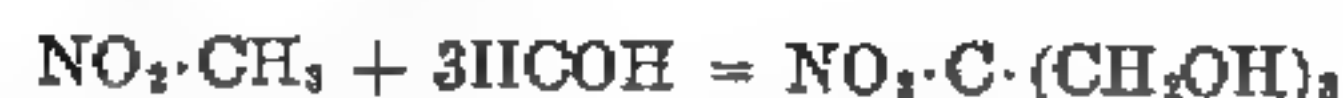
This compound is very interesting from the explosive point of view. It is equivalent to nitroglycerine and nitroglycol in explosive strength and brisance. It is both a nitric ester and a nitrocompound. It is the product of the nitration of nitroisobutylglycerine, a condensation product of nitromethane and formaldehyde. On detonation it

decomposes like nitroglycol into water, carbon dioxide and nitrogen, leaving no residue:



and has an energy exceeding even that of nitroglycerine. This compound was described by Hofwimmer.³⁰

Nitroisobutylglycerine is formed by the condensation of 1 molecule of nitromethane with 3 molecules of formaldehyde in the presence of potassium bicarbonate:



It crystallizes in needles or prisms, melting at 149°C. It is readily soluble in water and alcohol, but difficultly soluble in ether.

To prepare it one part of nitromethane is mixed with 4 parts of 40 per cent formaldehyde and about 1 gram of potassium bicarbonate added. After a short time the condensation occurs with violent boiling. According to other sources of information it must first be gently heated and then quickly cooled to temper the reaction. After evaporation in a vacuum the crude alcohol remains as a mass of crystals. The yield of crude product is about theoretical, or 247 parts from 100 parts of nitromethane. According to Hofwimmer this is then purified by sucking a little alcohol through it, but according to others it is better to recrystallize from amyl alcohol or amyl acetate at 90°C. The yield is 70 per cent of crude product, and has a melting point of 149°C.

Nitration. Esterification is done with the same mixed acids in about the same proportions as with glycerine, but less heat is evolved than with the latter.³¹ The crystals dissolve easily, and the oily ester separates readily and is purified like nitroglycerine. In order to avoid the formation of emulsions it is best to wash with very dilute soda solutions at moderate temperatures. When using a not absolutely pure alcohol an emulsion can form very easily on washing, and the ester gives up water very slowly. The yield is about 150 to 151 parts of the ester from 100 parts of the alcohol, the theoretical being 189.4, or about 80 per cent of theory. The nitrogen content is 19.44 per cent, of which 14.59 per cent is nitrate nitrogen. The figure 14.56 per cent was found by the Lunge nitrometer.

Properties of nitroisobutylglycerine trinitrate. This is a thick yellow oil, more viscous than nitroglycerine, odorless, and having a burning taste. Its specific gravity is 1.68 according to Hofwimmer. It is less volatile than nitroglycerine and has less tendency to cause headache. The crystallization tendency at low temperatures is

³⁰ Z. Schiess- u. Sprengstoffw. (1912), p. 43.

³¹ See English patent 6447 (1914).

slight. It is insoluble in water, but very soluble in alcohol, ether, benzene and chloroform, and insoluble in benzine, like nitroglycerine.

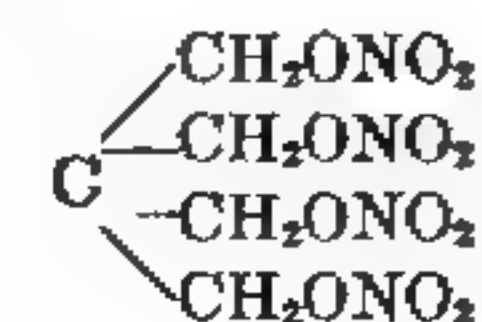
Chemical stability. On heating to temperatures of 70 to 80°C. the chemical stability is not less than that of nitroglycerine.

On igniting it burns quietly, with a light, blue-green flame, and explodes on heating above 180°C., after evolving red fumes.

Under the falling weight it detonates almost as easily as nitroglycerine. The 2 kg. weight causes detonation at 2 cm. with nitroglycerine and at 6 cm. with nitroisobutylglycerine trinitrate. The gelatinizing powers on collodion nitrocotton are appreciably less than those of nitroglycerine, even when hot.

Explosive strength. This is very similar to that of nitroglycerine. A 75 per cent kieselguhr mixture gave a lead block expansion of 325 cc., as compared to 305 cc. for nitroglycerine. Its 93 per cent blasting gelatine gives a somewhat lower expansion than when using nitroglycerine, 580 cc. as against 600 cc., since the oxygen excess of the nitroglycerine burns the collodion nitrocotton completely, so that in this case the total oxygen balance is more favorable and the heat of combustion higher. The heat of explosion of nitroisobutylglycerine trinitrate was determined experimentally as 1707 Calories per kilogram at constant volume and water liquid, as compared to 1595 Calories for nitroglycerine, so that the energy content of the former is therefore about 7 per cent higher. Practically, the use of this high grade explosive oil as a substitute for or replacement of nitroglycerine can only be considered when a sufficiently cheap method of producing nitromethane is discovered. The previously known processes do not give sufficiently high yields.³²

NITROPENTAERYTHRITE (PENTAERYTHRITE TETRANITRATE)



Of the solid esters of nitric acid, nitropentaerythrite has the most promise of practical use because in contrast to its closely related homologues, erythrite tetranitrate and nitromannite, it has a high chemical stability and is not too sensitive to mechanical influences.

³² German patent 294755 and Swiss patent 74333, on the preparation of nitromethane from NaNO_2 and sodium methylsulphate.

It has been proposed as an addition to smokeless powders³³ to raise their flammability and ease of combustion, and as a filler for blasting caps in place of or in mixture with tetranitromethyl aniline (tetryl) or trinitrotoluene,³⁴ where on account of its energy content which is higher than that of the aromatic nitrocompounds it would exert a greater initiating effect. Its disadvantage in this connection has been up to the present time a too great sensitiveness on pressing.

Furthermore, according to Jean Harlé, Rouen, German patent 336280 (1914), it may serve as a filler for cordeau detonant, either alone or mixed with fusible aromatic nitrocompounds.

For general use as an explosive or explosive component, for example in place of nitroglycerine for improving the ease of detonation, the relatively high price has been a disadvantage up to the present time, because both the synthesis of the raw material and the conversion into the ester are not sufficiently developed.

PENTAERYTHRITE, $C(CH_2OH)_4$

This is a quadrivalent alcohol formed by the condensation of 1 molecule of acetaldehyde with 4 molecules of formaldehyde in the presence of slaked lime, forming formic acid as a by-product, in dilute aqueous solution:



The synthesis was first described by Tollens and Wigand³⁵ in 1891, and Rave and Tollens³⁶ in 1893. Stettbacher³⁷ described it at length. Theoretically 100 parts of acetaldehyde give 309 parts of pentaerythrite and 104 parts of formic acid with 273 parts of formaldehyde and 40 parts of water. According to Stettbacher about 65 per cent of theory was obtained in preparing the crude product.

The process is as follows: 1940 grams of formaldehyde, or 4.85 kg. of a 40 per cent solution, and 600 grams of acetaldehyde (1 kg. of 60 per cent) commer-

³³ German patent 81664 (1894), *Rhein.-Westf. Sprengstoff A.-G.*

³⁴ German patent 265025 (1912); English patent 11809 (1913); French patent 451925 (1912), see also *Jahresber. d. Mil.-Vers. Amts*, 3, 13 (1896).

³⁵ *Ann.* 265, p. 318.

³⁶ *Ann.* 276, p. 58.

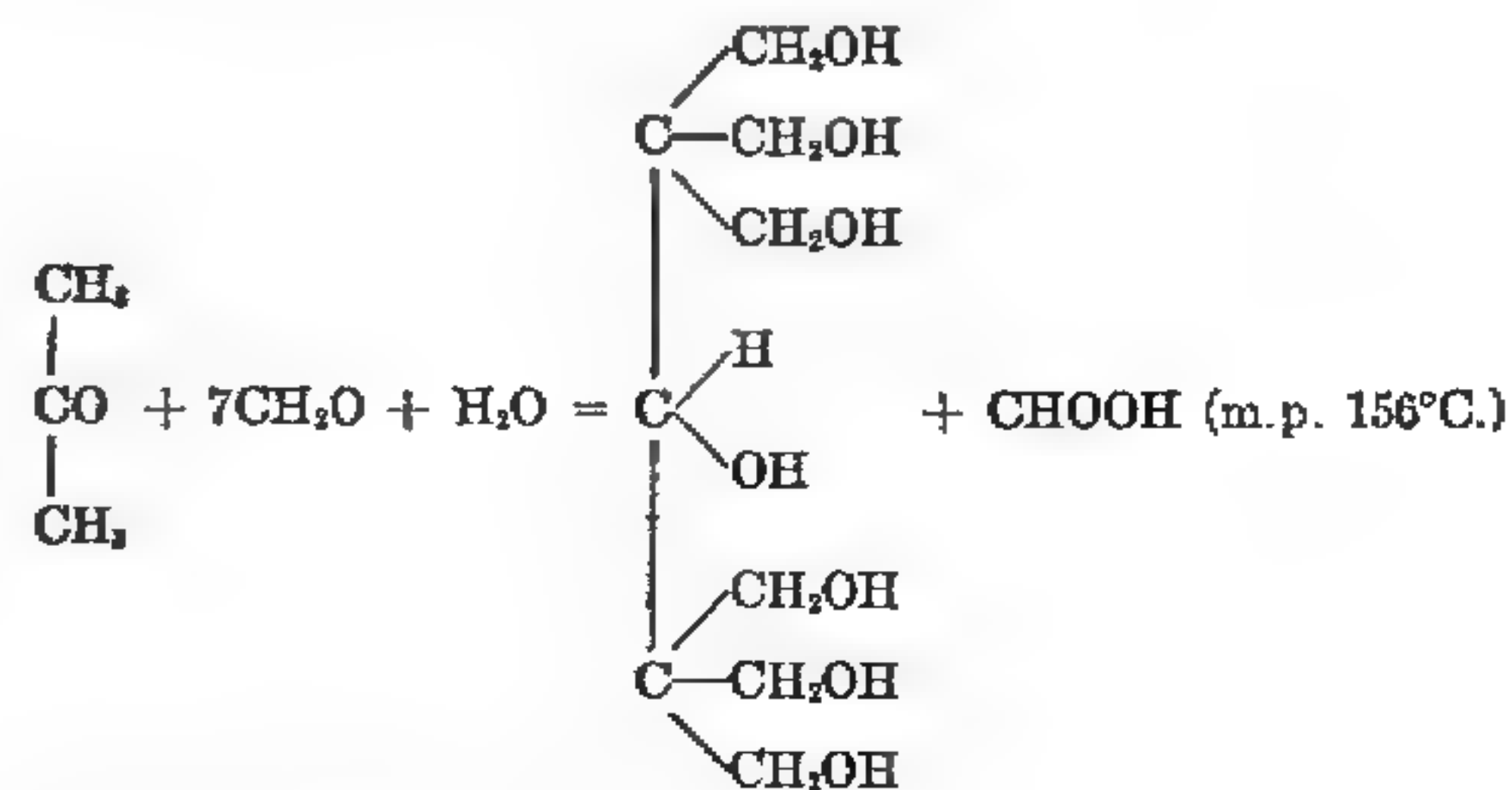
³⁷ *Z. Schiess- u. Sprengstoffw.* (1916), p. 182.

cial aldehyde) are dissolved in 90 liters of water containing 1600 grams of slaked lime in suspension. The solution is in a wooden cask which can be closed, since no pressure changes are encountered in the reaction. The cask is rolled about several times a day in order to bring the lime into sufficient contact with the solution. After about three weeks the reaction is complete. The solution is syphoned or filtered off and the calcium formate precipitated by oxalic acid, the alkaline reaction changing to acid and the brown color changing to yellow. The oxalate is allowed to settle, and the water is driven off under diminished pressure. The crystals obtained on cooling are centrifuged or drained from the syrupy mother liquor. A mixture like the above gives about 1200 grams of crude pentaerythrite having a melting point of 235 to 240°C.

For further purification the brown, crude product is stirred with a little alcohol and sucked dry on a filter, leaving the pentaerythrite perfectly white, and after several recrystallizations from water an absolutely pure product is obtained. For nitration this recrystallization is not necessary. Pure pentaerythrite forms tetragonal crystals melting at 253°C. It dissolves in 18 parts of water at 15°C.

An improvement in the production of pentaerythrite is disclosed in German patent 298932 (1914), issued to the Rhein.-Westf. Sprengstoff A.-G., in which the precipitation of the calcium formate by oxalic acid or sulphuric acid, with the subsequent difficult recovery of the free formic acid, is avoided, and instead the calcium formate, whose solubility changes very little with change of temperature as compared to the pentaerythrite, is thrown out by the proper hot concentration and so obtained as a by-product, filtered hot, and then on cooling the pentaerythrite is separated by crystallization.

For the similar synthesis of enneheptite from acetone and formaldehyde by water and slaked lime see Tollens; *Ann.* 289, page 47.³⁸



³⁸ German patent 286527 (1913), to E. v. Herz, on the use of anhydroenneheptite pentanitrate as a blasting cap charge.

Nitropentaerythrite

Preparation.³⁹ Mixed acid is not suitable for the nitration of this compound. On adding the latter to mixed acid the finely divided tetranitrate is not obtained, but instead a tough product difficult to purify and of low stability. On the other hand, pentaerythrite dissolves in a large excess of concentrated nitric acid, with partial esterification, which is completed by the gradual addition of concentrated sulphuric acid. One hundred grams of 94 per cent nitric acid at 25 to 30°C. dissolves only about 4 to 5 grams of pentaerythrite to a clear solution. If more is added, or if the acid is too cold the ester precipitates out as crystals. If the temperature is allowed to rise too high, in order to get more into solution, the charge takes fire very easily. It is best to operate as follows:

One hundred grams of finely powdered pentaerythrite is gradually dissolved in 400 cc. of nitric acid of a specific gravity of 1.52, with good cooling to 25 to 30°C. Theoretically 185.3 grams of HNO₃ is required, so that the above is a triple excess. Toward the end of the nitration the difficultly soluble nitrate partly separates. By the gradual addition of 400 cc. of concentrated sulphuric acid of a specific gravity of 1.84 and cooling, it is completely precipitated. It is allowed to stand for an hour and sucked dry on a filter, the acid being displaced first with a 50 per cent sulphuric acid and then with water. The last traces of free acid are removed by washing with a dilute soda solution. The theoretical yield is 232.5 grams. The yield of crude product amounts to 85 to 90 per cent of theory, according to the degree of purity of the pentaerythrite used. The crude product is not sufficiently stable chemically, since it still encloses traces of acid which cannot be separated by heating with water, even when alkalis are added. The iodine test is only a few minutes. For complete purification it is dissolved in a little hot acetone, some ammonium carbonate added, and the solution filtered through a hot water filter into twice its volume of 90 per cent alcohol, precipitating absolutely pure nitropentaerythrite in fine needles. The yield of the pure product is about 90 per cent of the crude used, and about 85 per cent of theory.

Properties. Pure nitropentaerythrite melts at 138.5°C. according

³⁹ Vignon, Gerin, C. R., 133, p. 590; also Stettbacher, *loc. cit.*, and German patent 265025 (1912).

to Will,⁴⁰ forms well defined crystals, and has an extraordinary chemical stability. It is insoluble in water, slightly soluble in alcohol and ether, and readily soluble in acetone. It withstands the iodine test at 80°C. for hours and can be stored at temperatures of 50 to 100°C. for a long time without decomposition.

As regards its chemical stability it exceeds its homologs, nitroerythrite and nitromannite, considerably, as well as nitroglycerine and nitrocellulose, probably due to its peculiar molecular structure. In the polyvalent, aliphatic nitric esters having a chain structure of the carbon atoms, the chemical stability as a rule diminishes with the length of the carbon chain. Thus nitroglycerine is less stable than nitroglycol, and nitroerythrite and nitromannite less stable than nitroglycerine, while the still higher molecular nitrocellulose assumes a special position in which it must be remembered that it is not a pure ester and that not all of its hydroxyl groups can be esterified by nitric acid. The highest nitrated nitrocellulose is a mixture of hexa- and pentanitrocellulose, with about 13.5 per cent nitrogen, containing 5 to 6 nitric acid radicals to a chain of 12 carbon atoms, while with nitroglycerine containing 18.50 per cent nitrogen and nitromannite with 18.58 per cent there is a nitric acid radical to each carbon atom. The lower stability of nitroglycerine, and particularly nitromannite, as compared to nitrocellulose, can therefore be explained by the greater accumulation of nitric radicals attached to the carbon chain.

A peculiar position is assumed by nitropentaerythrite as regards stability. It contains 4 nitric acid radicals to 5 carbon atoms, and 17.74 per cent nitrogen. Stettbacher⁴¹ not improperly attributed this phenomenon to the peculiar position of the 4 methoxyl groups about the central quaternary carbon atom.

Above the melting point decomposition sets in. A small amount of nitrogenous gases begins to split off after one-half an hour at 140 to 145°C. In a bath of Wood's metal 0.2 gram of nitropentaerythrite at 175°C. and above gives off light yellow vapors, from 190°C. and up red fumes, and at about 205°C. there is a weak deflagration.

Flammability. Nitropentaerythrite is difficult to ignite. It does not take fire from the spit of a fuse or the flame of a match. If

⁴⁰ The author found the melting point to be 140 to 141°C.

⁴¹ Z. Schiess- u. Sprengstoffw. (1916), p. 112.

ignited by a greater heat than this it burns quietly when in small quantities.

Stability on heating. Pure nitropentaerythrite can be stored in covered weighing bottles at 75°C. for weeks without decomposition. Even after several days at 90°C. there is no acid reaction, and the loss in weight is only 0.1 per cent.

Sensitiveness to mechanical effects. Nitropentaerythrite is relatively insensitive to friction. On rubbing in a rough porcelain mortar there is a loud crackling but no real detonation. On the other hand, the sensitiveness to shock is relatively high, although less than that of nitroglycerine and guhr dynamite. Under the 2 kg. weight nitropentaerythrite detonates at 20 cm. fairly regularly with a loud report, but only occasional detonations occur at 15 cm. and 10 cm.

Explosive character and strength. In view of the small oxygen deficiency of 10.1 per cent and the probable decomposition according to the following equation:



a fairly high explosive strength would be expected. The calculated heat of explosion of nitropentaerythrite, based upon a heat of formation of 131.2 Calories, is 1522.5 Calories per kilogram with water liquid, and 1403.2 Calories per kilogram with water gaseous, or 95 per cent of that of nitroglycerine. In the lead block 10 grams under sand tamping gave an expansion of about 500 cc. Nitropentaerythrite thus belongs to the strong explosives.

	cc.
10 grams nitropentaerythrite under water tamping.....	560
10 grams liquid nitroglycerine under water tamping.....	about 600

The expansions are about as 93.3:100. Their relation therefore agrees rather well with their energy contents, or 1403.2:1485 as 94.5:100.

Moreover the sensitiveness to initial impulse is extremely high, higher than that of the highly nitrated aromatic nitrocompounds like tetryl (tetranitromethylaniline), so that nitropentaerythrite has been considered as a charge of blasting caps in place of aromatic nitrocompounds. For example, tetryl requires more than 20 mg. of lead azide to ensure its detonation, while 1 mg. of lead azide suffices for nitropentaerythrite.

The very high sensitiveness of nitropentaerythrite toward initial impulse is also shown by the fact that the weakest blasting cap, a No. 1, gives almost the same expansion in the lead block with this explosive as does the usual No. 8 cap. (See table 18.)

Lead crusher test. Nitropentaerythrite gives an extraordinary crushing effect on the lead cylinder. One hundred grams of it compresses the cylinder 22 mm. and deforms it considerably.

Velocity of detonation. The velocity of detonation is also very high. The author found, in an iron pipe 25 mm. internal diameter, at a density of 0.85, i.e., slight compression of the nitropentaerythrite, a velocity of 5330 meters per second.

TABLE 18
Comparison of expansion by different blasting caps

	WITH NO. 8 CAP	WITH NO. 1 CAP
	cc.	cc.
Net expansion.....	500	460
Deduction for the cap.....	30	5
	470	455

On the other hand Kast found with highly compressed material of a density 1.62 more than 8000 meters per second, or a velocity of detonation of the highest order.⁴²

NITROMANNITE (MANNITE HEXANITRATE)



Nitromannite is the homologous nitric ester of nitroglycerine of the highest molecular weight which has been investigated for commercial use. On account of its ease of detonation, high energy and relatively low sensitiveness to mechanical effects even Sobrero recommended it as a substitute for mercury fulminate in priming compositions such as in percussion caps.⁴³ However, the investigation undertaken by the Royal Arsenal at Turin in comparison with mercury fulminate apparently came to nothing.

⁴² Z. f. angew. Chem. (1923), p. 74.

⁴³ C. R. (1847), p. 121; and Molinari and Quartier, "Notices sur les Explosifs en Italie," Mailand 1913 bei Hoepli, p. 16; Die Entdeckung des Nitromannites.

Then nitromannite was more closely investigated as to its explosive properties by Berthelot⁴⁴ and Sarrau and Vieille.⁴⁵ Further work was done by Domonte and Ménard,⁴⁶ Strecker,⁴⁷ Sokoloff,⁴⁸ and particularly by Wigner.⁴⁹

Nitromannite was obtained by the esterification of *d*-mannite, which is widely distributed in the vegetable kingdom and obtained particularly from the juice of the manna.⁵⁰ The *d*-mannite crystallizes in needles or prisms, melting at 166°C., and is rather soluble in water.

This hexavalent alcohol can be nitrated without difficulty. In theory about as much nitric acid is required as for the nitration of glycerine, or 207.7 parts of HNO₃ for 100 parts of mannite as against 205.4 parts of HNO₃ per 100 parts of glycerine.

Introducing the voluminous mass of crystals into the mixed acid is not recommended because the product cakes together and is thus prevented from being thoroughly nitrated. It is better to dissolve 1 part of mannite in 5 parts of concentrated nitric acid of a specific gravity of 1.51 with good cooling, and while still cooling to add gradually to the clear solution 10 parts of 66° Bé sulphuric acid, throwing down the nitromannite as a thick soup of crystals, which is sucked dry on a filter which has been previously hardened by treating with mixed acid. It is then washed with water, and neutralized with dilute sodium bicarbonate solution. The crude hexanitate is recrystallized from boiling alcohol by using a hot water heated funnel, to get it absolutely pure. If the mother liquor is heated to boiling and water added until a turbidity occurs the rest of the nitromannite separates almost completely on cooling. The yield is 232.5 per cent of the mannite used, the theoretical being 248.35 per cent, or a 93.6 per cent yield. In the Lunge nitrometer the crude nitromannite gives a nitrogen content of about 18.2 per cent, and that recrystallized from alcohol the theoretical 18.58 per cent.

⁴⁴ Berthelot, *Sur la force des matières explosives*, II, p. 204.

⁴⁵ *Mem. poudre salp.*, II, p. 126 (1884-89).

⁴⁶ *C. R.*, 24, p. 89, 390 (1847).

⁴⁷ *Ann.*, 73, p. 59 (1850).

⁴⁸ *Ber.*, 12, p. 688, 698 (1873).

⁴⁹ *Ber.*, 36, p. 956 (1903).

⁵⁰ For occurrence and preparation of manna and mannite see *Beilstein Handbuch*, 4 ed., vol. I, p. 534.

*Properties.*⁵¹ Pure nitromannite melts at 112 to 113°C. It has a specific gravity of 1.604, but when recrystallized from alcohol as fine crystals it is a voluminous mass. It is insoluble in water, very soluble in ether and hot alcohol, but only slightly so in cold alcohol.

Chemical stability. Even with the pure product twice recrystallized from alcohol the chemical stability is relatively low at high temperatures, apparently due to the chemical constitution or accumulation of nitric acid radicals on the open carbon chain.

While the low-molecular nitric esters like nitroglycol, methylglycol dinitrate, trimethylene glycol dinitrate, etc., endure heating for days at a time in a covered weighing glass at 75°C. without decomposing, and even nitroglycerine only begins to give off acid vapors under these conditions after some days, nitromannite at 75°C. evolves nitrous gases after a few hours and decomposes.

Nitromannite is not very flammable, and is only fused locally by the spit of a fuse, without being ignited. On the other hand with a somewhat longer contact with a flame, as from a match, which gives a local overheating, detonation occurs readily with a sharp report.

On gradually heating a small sample in a beaker in a bath of molten metal the material decomposes even at 150°C. and gives off copious red fumes, without deflagrating. With somewhat larger quantities there is a deflagration at 160 to 170°C.

Sensitiveness to shock. This is rather high, and about the same as that of nitroglycerine. Under the 2 kg. weight detonation occurs at a drop of 4 cm. It is also rather sensitive to friction.

Energy content. The oxygen balance of nitromannite is +7.1 per cent. It decomposes according to the following equation:



and with a heat of formation of 185 Calories its calculated heat of explosion is 1468 Calories per kilogram at constant volume and water liquid, or 92 per cent of that of nitroglycerine, while Sarrau and Vieille⁵² found 1512 experimentally. From this the temperature of explosion can be calculated as 3340°C.

Velocity of detonation. This has been measured by Berthelot at a density of loading of 1.5 and at about 4 mm. diameter as 7000 meters

⁵¹ *Beilstein, Handbuch*, 4 ed., vol. I, p. 543.

⁵² *C. R.*, (1881), 93, p. 269.

per second.⁵³ Without any particular compression in an iron pipe 25 mm. internal diameter and 5 mm. walls, at a density of 0.9 the author found by the Dautriche method a velocity of detonation of about 5600 meters per second. With highly compressed material Kast found 8260 meters per second at a density of 1.73 and a diameter of 12.8 mm.⁵⁴

On account of the high price of the raw material nitromannite as a brisant explosive or as an addition to other explosives has not come into use. As a cap charge it could be considered only in place of other base charges, but not as a top charge, because it has too low a sensitiveness to flame and is not an initiator. A top charge of mercury fulminate or lead azide can be used to detonate it. Any such use is difficult on account of its high sensitiveness to shock. Moreover its chemical stability does not seem to be sufficient for any practical use.

GLYCERINE-SUGAR NITRATE

Although a discussion of the varieties of nitrosugar can no more be included in this book than the nitric esters of the other carbohydrates, such as nitrocellulose and nitrostarch, since it deals only with nitroglycerine and homologous nitric esters of the pure alcohols, in closing there should not be left unmentioned a product having a great similarity to nitroglycerine, used as such in the United States and Germany during the World War for a time, and which has attained a certain degree of importance.⁵⁵ This is a solution of nitrated saccharose in nitroglycerine, obtained by the nitration of ordinary sugar, refined cane or beet sugar, dissolved in glycerine.

The pure nitrates of saccharose are very difficult to purify on account of their peculiar physical properties, and to bring into a state of good stability. They soften on gentle heating and pass into a peculiar resinous, tough condition, so that the traces of decomposition products which facilitate the decomposition catalytically cannot escape. Furthermore their chemical stability appears to be lower than that of nitroglycerine on the basis of chemical structure. In a state of solution, on the other hand, for example in nitroglycerine, the

⁵³ *Ann. chim. phys.*, 6, p. 556 (1885).

⁵⁴ *Z. angew. Chem.*, (1923), p. 74.

⁵⁵ The use of this was started in the United States in 1911 and has continued.

—TRANSLATOR.

nitrosugars can be comparatively easily stabilized to a high degree, making a practical use of this mixture possible.

Björkmann⁵⁶ nitrated a solution of 25 parts of glucose in 75 of glycerine. English patent 17221 (1911) issued to Cocking and Kynoch Ltd. protected a process of nitrating a mixture of any convenient composition of glycerine and ordinary sugar, purifying the product of the nitration when in a state of low viscosity, as in solution in nitroglycerine, and using it as an explosive.⁵⁷ Finally United States patent 1149487 (1915) describes the nitration of glycerine-sugar solutions. In the United States the duPont de Nemours Powder Company, even before the World War, used an explosive oil called "nitrohydrene," obtained by the nitration of a solution of 20 parts of sugar in 80 parts of glycerine, as a substitute for nitroglycerine. This is said to have caused a saving in the expensive glycerine or to have made the glycerine go further.

In Germany the scarcity of glycerine during the World War led to the use of the same process, and this type of nitroglycerine, so to speak, was used for some time in mining explosives. However, since the saving in glycerine did not amount to more than 12 to 14 per cent and the acid consumption was higher, on account of the unfavorable nitrating conditions of the sugar, the lower degrees of nitration of the sugar being washed out, it was given up.

Preparation of the glycerine-sugar solutions

Finely pulverized refined sugar dissolves rather easily in hot glycerine, while large crystals dissolve slowly.⁵⁸ Solutions containing 80 parts of glycerine to 20 parts of sugar, and 75 glycerine to 25 sugar can be easily prepared, but in the proportion of 70:30 solution is not complete, and in this case the syrup obtained is so viscous even when hot that its use involves practical difficulties. Moreover the nitroglycerine-nitrosugar solution obtained is the more viscous and difficult to stabilize the higher the sugar content of the glycerine.

Denaturing sugar. If it is a question of avoiding a government

⁵⁶ English patent 2483 (1880).

⁵⁷ Also English patent 2836 (1911).

⁵⁸ The ordinary table grade of refined sugar is used in the United States, a few per cent of refined glucose being added to prevent crystallizing when shipped out during cold weather.—TRANSLATOR.

tax on edible sugar or to protect the sugar from theft, denatured sugar can be used for nitration. The addition of 0.2 to 0.3 per cent of cresol, for example, makes the sugar inedible and does not interfere with the nitration in any way. The small amount of cresol, 0.06 in an 80/20 glycerine-sugar solution if 0.3 per cent cresol is used in the sugar, is nitrated, and the nitrocresol remains in the nitroglycerine or dissolves in the spent acids.

Nitration. Nitration is done in exactly the same way and with the same acids and quantities of acids as with glycerine, and shows no peculiarities. The separation is also smooth.

Washing. This, on the other hand, requires a great deal of attention, as the product forms emulsions easily, which when once formed are very difficult to break. By using moderate air agitation formation of emulsions can be avoided, and after the soda wash moderately concentrated common salt solutions (about 10 per cent) can be used to facilitate the separation of the wash waters and oil.

Naturally these provisions require a longer period of stabilization than with pure nitroglycerine. As a rule the soda wash must be somewhat more intensive than with nitroglycerine to obtain the same Abel heat test. Frequently repeated treatment with soda is necessary. The higher viscosity of the oil is responsible for this. However, it is not difficult to obtain an Abel test of twenty-five minutes at 72°C., and sixteen to eighteen minutes at 82°C.

Yields. With the 80:20 mixture the yields are about 210 per cent with a nitrating temperature of 20 to 25°C., whereas nitroglycerine gives 227 per cent, and about 214 per cent at 15°C., nitroglycerine giving 230 per cent. With the 75:25 mixture 206 per cent is obtained at 25°C., and 210 per cent at 10°C.

Nitrogen content. With the 80:20 mixture the nitrogen content of the oil is 18.05 to 18.10 per cent, and with the 75:25 mixture 17.90 to 17.95 per cent.

Viscosity. The oils are appreciably more viscous than nitroglycerine. For example, the product of the nitration of the 75:25 mixture is more than twice as viscous as nitroglycerine. The time taken for 5 cc. to run out of a 10 cc. pipette at 20°C. is:

Nitroglycerine.....	sec. 13
Nitrohydrene, 80/20.....	21
(or 86 per cent nitroglycerine-14 per cent nitrosugar)	
Nitrohydrene, 75/25.....	34
(or 82 per cent nitroglycerine-18 per cent nitrosugar)	

Specific gravity. The specific gravity is somewhat higher than that of pure nitroglycerine, for example:

Specific gravity at 20°C.

Nitroglycerine.....	1.596
Nitrohydrene 80/20.....	1.605
Nitrohydrene 75/25.....	1.612

Degree of nitration of the nitrosugar. If a nitroglycerine yield of 225 per cent is assumed, the 210 per cent of nitrohydrene obtained would correspond to 180 parts of nitroglycerine and 30 parts of nitrosugar. Assuming a heptanitrosugar containing 14.9 per cent nitrogen, such a mixture consisting of 86 per cent nitroglycerine and 14 per cent nitrosugar, would theoretically have a nitrogen content of 18.00 per cent. Assuming an octanitate with 15.95 per cent nitrogen it would be 18.10 per cent. With this small difference and the unavoidable experimental error in analysis, it must remain uncertain what degree of nitration is assumed by the sugar in general. Here the yield on sugar amounts to only about 150 per cent. The theoretical yield for heptanitate is 192 per cent, but it must be remembered that the conversion of sugar into the highly nitrated stage is in no way complete and that portions of the lower degrees of nitration are formed, which it is possible are more easily soluble and remain in part dissolved in the acids and are in part washed out during the washing process.

Explosive strength. The explosive strength of nitrohydrene comes very close to that of nitroglycerine. With 10 grams in a glass tube under sand tamping the author found a lead block expansion as follows:

Nitroglycerine.....	550 cc., 100 per cent
Nitrohydrene 80/20.....	533 cc., 97 per cent
Nitrohydrene 75/25.....	514 cc., 94 per cent

and 10 grams under water tamping gave:

Nitroglycerine.....	595 cc., 100 per cent
Nitrohydrene 80/20.....	560 cc., 94 per cent
Nitrohydrene 75/25.....	535 cc., 90 per cent
92 per cent nitroglycerine blasting gelatine.....	595 cc.
92 per cent nitrohydrene 80/20 blasting gelatine.....	615 cc.
75 per cent nitroglycerine guhr dynamite.....	320 cc.

75 per cent nitrohydrene 80/20 guhr dynamite.....	320 cc.
65 per cent nitroglycerine gelatine dynamite.....	385 cc.
65 per cent nitrohydrene 80/20 gelatine dynamite.....	395 cc.

Chemical stability. The chemical stability of nitrohydrene is considerably less than that of nitroglycerine, particularly at high temperatures. If after stabilizing to a thirty minute potassium iodide test it is stored for a long time, the test gradually diminishes, even at room temperatures, and after weeks or months it becomes acid, and finally starts to decompose. The higher the temperature of storage the more rapid this process. (See table 19.) Nitroglycerine withstands these temperatures for weeks at a time without decomposition. At 75°C. nitrohydrene decomposes after one day, while

TABLE 19

Chemical stability of nitrohydrene

Storage at 45°C., 10 grams in loosely covered weighing bottles

	80/20 NITROHYDRENE, ORIGINAL TEST TWENTY-FIVE MINUTES	75/25 NITROHYDRENE, ORIGINAL TEST EIGHTEEN MINUTES
Acid reaction after.....	10 days	5 days
Yellow vapors after.....	18 days	10 days
Complete decomposition after.....	24 days	12 days

with nitroglycerine decomposition does not set in until several days have passed.

The German railroad regulations for explosives require that whole cartridges withstand storage at 75°C. for forty-eight hours without any visible sign of decomposition products such as nitrous gases, a requirement easily fulfilled by nitroglycerine preparations like guhr dynamite and blasting gelatine, provided that thoroughly stabilized nitroglycerine is used.

Guhr dynamite and gelatine, made with nitrohydrene, when in cartridges, on the other hand decomposed after twenty-four to thirty hours at 75°C. and evolved red fumes. However, cartridges of gelatine dynamite, carbonit, and nobelit containing nitrohydrene in place of nitroglycerine withstood this test for forty-eight hours without decomposing, and were stored at 50°C. for more than six weeks, finally showing only a slight reddening of a moist blue litmus

paper. These explosives contained considerable wood meal or cereal meal, both of which are constituents apparently acting as stabilizers, since they absorb the first traces of decomposition products or react chemically and destroy them. This avoids the catalytic acceleration of the decomposition by the decomposition products when the latter are retained in the mass, and the life of the explosive is thereby considerably increased.

Diphenylamine as a stabilizer. Better still are very small additions of diphenylamine, which is admirably suited for the stabilization of smokeless powder, since it readily takes up the nitrous acid.

Nitrohydrene 80/20 or 75/25, containing only 0.1 to 0.2 per cent of diphenylamine, was stored for seventy-five days at 55°C. without undergoing decomposition. The samples merely showed a coloration and became dark green, a phenomenon which also occurred but to a less extent with a check sample of nitroglycerine containing the same quantity of diphenylamine. After seventy-five days the nitroglycerine still had a slight odor of diphenylamine, but the nitrohydrene smelled slightly acid, somewhat like sour milk, but not like nitrous or nitric acid.

Similar samples of 100 grams each of the above nitrohydrene containing 0.1 per cent diphenylamine have been stored by the author for more than eight years in diffuse daylight at room temperatures, about 20°C. So far they have remained unchanged, have no acid odor and show no signs of decomposition. Their nitrogen content is still 18.03 and 17.77 per cent for the 80/20 and 75/25, respectively, the effect of the diphenylamine upon the analytical results having to be taken into consideration. From this it is evident that nitrosugar dissolved in nitroglycerine, although its stability does not reach that of the latter, is sufficiently stable for practical purposes, particularly in the presence of stabilizers.

Any possible commercial use of this fact in the future will be a question of the price difference between glycerine and sugar, together with the most advantageous and improved nitrating methods.

Nitration of glycol-sugar solutions

Tests on the nitration of solutions of sugar in glycol gave the following results:

At 80 to 90°C. solutions of 25 parts of sugar and 75 of glycol, or

even 30/70 solutions were formed without difficulty. On long standing at ordinary temperatures a portion of the sugar crystallized out. The 80/20 solutions remained liquid when cold, with only a slight separation.

Nitration and washing corresponded to conditions with glycerine-sugar mixtures.

Yields:	per cent	Nitrogen content per cent
80/20 Glycol-sugar.....	199.5	17.9
75/25 Glycol-sugar.....	195.0	17.8

With the same acids and at the same temperature glycol gives 216.5 per cent nitroglycol. It is evident from the nitrogen calculation that here also the nitrosugar is nitrated to the hepta stage.

Nitration of glucose-glycerine, and lactose-glycerine solutions

Solutions of grape sugar or milk sugar can be nitrated with results similar to those obtained with glycerine-saccharose solutions. Grape sugar dissolves in glycerine more readily than does milk sugar or beet sugar, and with it solutions of 40 parts of grape sugar to 60 parts of glycerine can be formed. On the other hand, milk sugar is considerably more difficult to dissolve in glycerine than is beet sugar. A solution of 20 parts of it in 80 parts of glycerine can be formed at 100 to 105°C., but on cooling it crystallizes to a soup of crystals.

Nitration of glucose-glycerine solutions form mixtures of nitroglycerine and pentanitroglucose, or an oil containing 18.20 per cent of nitrogen in the case of an 80/20 mixture. Lactose-glycerine solutions on nitration form mixtures of nitroglycerine and octanitrolactose.

These mixtures also do not differ appreciably in explosive strength from that of nitroglycerine. In stabilization, particularly with the glucose solutions, the formation of emulsions should be even more carefully avoided than in the case of the saccharose solutions.

Note by translator. In the United States the Trauzl lead block as a test for explosives has not been employed for many years. In its place the ballistic mortar has been used by the industries, and the ballistic pendulum by the Bureau of Mines. The former determines strength of an explosive by the recoil of the suspended mortar as it discharges a projectile, the latter measures the strength of an explosive by the swing given to a suspended cannon which receives the tamping and gases issuing from a mortar. The latter is not used widely by the industries on account of the expense of operation.

TABLE 20
Table of the properties of nitroglycerine, its related and homologous nitric esters

COMPOUND	MOLECULAR WEIGHT	NITROGEN CONTENT per cent	MELTING POINT °C.	BOILING POINT °C.	SPECIFIC GRAVITY	VISCOSITY* seconds	OXYGEN BALANCE	MOLECULAR HEAT OF FORMATION calories	HEAT OF EXPLOSION, CALORIES PER KILOGRAM		LEAD BLOCK EXPANSION cc.	REMARKS
									H ₂ O gas	H ₂ O liquid		
Nitroglycerine.....	227.0	18.50	Labile + 2.8 Stable + 13.6	Decomposes 146° at 15 mm.	1.590 at 15°	12.5	+3.5	94.2	1,485	1,595	800	With water tamping
Dinitroglycerine.....	182.0	15.38	Hydrate + 26	156-160 at 15 mm.	1.610 at 15° Hydrate = 1.47	20.0	-17.6	116.7	1,201	1,304	500	With water tamping
Mononitroglycerine.....	137.0	10.22	α 58-59 β 54	174-175 with decomposition. 94 at 20 mm. 180 with decomposition 117.5 at 10 mm.	1.417 liquid at 15° α cryt. 1.53	Very viscous	-52.5	139.4	434	572	245	Crystalline, with sand tamping
Nitroglycide.....	110.0	11.78	Liquid at -20	176 with decomposition 88 at 15 mm.	1.352 at 20°	4.5	-60.5	51.4	745	824	430	With water tamping
Dinitrochlorohydrine.....	200.6	13.97	α + 5 β + 16.2	176 with decomposition 88 at 15 mm.	1.541 at 15°	7.0	-19.94	87.8	1,053	1,100	475	With water tamping
Nitrodechlorohydrine.....	174.0	8.05	Liquid at -20	147 with decomposition at 15 mm.	1.450 at 15°	5.0	-41.4	81.3	440	495	—	Can hardly be exploded
Acetyldinitroglycerine ...	224.0	12.50	Liquid at -20	—	1.412 at 15°	15.5	-42.86	165.6	857	715	200	With water tamping
Formyldinitroglycerine.....	210.0	13.33	Oily	Decomposes	—	Viscous	-22.9	149.9	1,009	1,069	—	—
Tetranitroglycerine.....	346.0	16.18	Liquid at -20	65.0	1.21 at 15°	4.0	-10.39	165.1	1,262	1,371	—	—
Methyl nitrate.....	77.0	16.20	Liquid at -20	87.0	1.12 at 15°	4.0	-61.6	39.6	1,490	1,612	615	With water tamping
Ethyl nitrate.....	91.0	15.40	Liquid at -20	110.5	1.08 at 15°	4.0	-99.0	48.5	713	816	345	With water tamping
Propyl nitrate.....	105.0	13.34	Liquid at -20	95 at 10 mm.	1.06 at 15°	4.0	-0.0	56.3	549	639	230	Absorbed in Kieselguhr
Nitroglycol.....	152.0	16.42	Liquid at -20	91-92 at 10 mm.	1.495 at 15°	5.0	-37.4	67.7	1,581	1,705	650	With water tamping
Mononitroglycol.....	107.0	13.09	Liquid at -20	103 at 10 mm.	1.348 at 20°	5.5	—	90.0	856	944	375	With water tamping
Trimethylene glycol dinitrate.....	166.0	16.88	Liquid at -20	92 at 10 mm.	1.393 at 20°	5.5	-28.9	79.1	1,138.5	1,252	540	With water tamping
Propylene glycol dinitrate.....	166.0	16.88	Liquid at -20	—	1.358 at 20°	5.0	-28.9	83.1	1,109	1,222	540	With water tamping
Nitroerythrite.....	302.0	18.56	Oily	Decomposes	1.68	Viscous	+5.3	130.5	1,414	1,508	—	—
Nitroisobutylglycerine trinitrate.....	286.0	19.59	—	—	—	—	±0.0	—	—	1,707	—	—
Nitropentaerythrite	316.0	N ₂ = 14.59 N ₂ = 17.74	140-141	—	1.728	—	-10.1	131.2	1,403	1,523	505	With sand tamping
Nitromannite.....	452.0	18.58	112-113	—	1.60	—	+7.1	185.0	1,376	1,468	560	With water tamping

Another difference in the United States is the requirement by the consumer of explosives of a much higher "gap test" between exploding cartridges than is prevalent in Europe, probably more than twice as high as a general average. Higher "gap test" means greater sensitiveness, and the latter means less chance of misfires when foreign material is accidentally placed between cartridges in the borehole.

Also, no blasting caps smaller than the No. 6 are sold in the United States, and there is a constantly growing consumption of the No. 8 size. This gives a larger margin of safety when using explosives which may not be up to standard, due to age or improper storage.

The nitrometer used for the determination of NO evolved from nitrates has a compensator bulb filled with dry air, so that barometer and temperature corrections need not be applied to the readings, the compensator exactly equalizing these. This makes for more rapid determinations.

The average size of cartridges in the United States is probably larger than in Europe. Probably about 80 per cent of the total explosives here are supplied in the form of $1\frac{1}{2}$ x 8 inch sticks, and the production of cartridges 5 and 6 inches in diameter by 8 to 16 inches long is constantly increasing, due to the growing demands of well-drilled quarry holes.

The consumption of cordeau is rapidly increasing for the same reason, as it gives more reliable simultaneous detonation of a large series of holes than do electric caps with their multiplicity of connecting wires.

A more astonishing development in the last few years has been the constantly increasing number of cartridges per 50-pound box, or the decrease in the density of the cartridge explosive. This has grown from a maximum of 270 $1\frac{1}{2}$ x 8 inch cartridges per 100 pounds a few years ago to 500 recently. This low density of explosive makes for a less concentration of the explosive at the back of the borehole in coal mining, and a greater distribution of pressure against the walls of the hole, making less fine dust and more lump coal. Another result has also been that a ton of coal has been produced by the use of these explosives with less actual explosive than formerly.

Greater limits of velocity of detonation of permissible explosives seem to be in use in the United States than in Europe. For example, permissible explosives as tested by the Bureau of Mines have velocities of detonation from 4640 feet per second (1,415 meters per second) to 13,680 feet or 4,155 meters per second.

PART III

NITROGLYCERINE EXPLOSIVES

CHAPTER XVIII

THE USE OF NITROGLYCERINE

About 1864 Alfred Nobel began to introduce nitroglycerine as an explosive on a large scale. Soon numerous accidents both in transportation and use forced consideration to be taken of means of avoiding the danger in handling the liquid nitroglycerine.

Transportation was in sheet metal cans, packed in boxes. Any leak in such a can was always a source of great danger, because of the high sensitiveness of the oil to shock, and any leakage was difficult to clean up on account of non-volatility and insolubility in water.

Mowbray, who was using nitroglycerine as an explosive at about this time in North America (Massachusetts) in the construction of the Hoosac Tunnel, met this transportation danger by furnishing the nitroglycerine in a frozen condition in sheet metal containers, in which it was thawed just before use. The probability of leakage or spilling was very much less, and the low sensitiveness to shock of the frozen nitroglycerine was an advantage. Such use continued in America for several years after the discovery of dynamite, and as Gutmann states, could only be uprooted with difficulty on account of the conservatism of the English race.

Nobel mixed the explosive oil with 15 to 20 per cent of anhydrous methyl alcohol, and thus reduced its sensitiveness to shock considerably. However, this was the only advantage of this inconvenient and little economical precaution. The methyl alcohol had to be washed out by water before use, which required an undesirable handling of the explosive oil just before use at the point of consumption. Other similar proposals to render nitroglycerine less sensitive for transportation received little attention for this reason.

In the blasting itself the liquid condition was a source of inconvenience and danger. It was difficult or almost impossible to load horizontal or upwardly inclined boreholes. The danger of spilling at the point of consumption was always present, and finally the nitroglycerine found its way into fissures in the rock, where it escaped explosion, and perhaps burned and formed injurious gases, or sub-

sequently exploded on removing the broken rock by a pick, or in drilling new boreholes in the vicinity, and so was a frequent source of accidents.

In England, as the result of the creation of a testing commission in 1874, the use of liquid nitroglycerine was absolutely prohibited, and such use disappeared also in Europe and only continued, as previously mentioned, in America.

Even in 1866 an accident at the Krümmel Plant revealed the absorption of nitroglycerine by kieselguhr to form a solid, plastic mass, and the preponderating and soon overwhelming use of nitroglycerine in the form of a powdery or plastic mass, which could be packed into paper cartridges and these in turn in cartons and boxes dates from this time. This formed an explosive which was safe for transportation, storage, handling and loading into boreholes in a very convenient manner.

From the crumbly, plastic mass formed of a mixture of nitroglycerine and kieselguhr, which first received the name of dynamite, the name spread to other brisant explosives containing nitroglycerine as the main component. Today in a broad sense the word dynamite is understood to cover all moist powdery, plastic or gelatinous explosives which contain nitroglycerine as the main explosive.

A second and no less significant use of nitroglycerine was found in the eighties of the previous century in its employment as a propellant, by the discovery of the artillery powders ballistit and cordite, smokeless powders containing nitroglycerine, which were horn-like, gelatinous masses consisting mainly of nitroglycerine and nitrocellulose. The enormous significance of this method of using nitroglycerine, and its irreplaceability in modern warfare, was only revealed by recent wars, mainly by the World War.

CLASSIFICATION OF NITROGLYCERINE EXPLOSIVES

In a stricter sense of the word the dynamites, or nitroglycerine explosives, will be divided for the purpose of convenience into the following groups:

1. *Dynamites*. (a) Dynamites with a chemically inactive base, like guhr dynamite. (b) Dynamites with a chemically active base, such as mixtures containing wood meal, charcoal, saltpeters, etc.

2. *Blasting gelatines*, or colloids of nitroglycerine and soluble nitrocellulose.

3. *Gelatine dynamites*, or gelatinous mixtures in which the blasting gelatine has added to it absorbents consisting of saltpeter and wood meal for the purpose of tempering its action.

4. *Low-freezing or non-freezing dynamites*, in which the nitroglycerine is either partially replaced by aromatic nitrocompounds, or wholly or partially replaced by related, explosive nitric esters such as dinitroglycerine, dinitrochlorohydrine, tetranitrodiglycerine or nitroglycol.

5. *Permissible dynamites* with nitroglycerine as the essential component or explosive. These, on account of special components, have the property of not igniting fire damp and coal dust. Here also there is a differentiation between powdery mixtures in which the nitroglycerine is merely absorbed, versus gelatinous mixtures in which the nitroglycerine has previously been converted to a gelatinous condition with collodion nitrocotton. The latter are called permissible gelatine dynamites. Naturally such explosives contain less nitroglycerine than the true dynamites and gelatine dynamites.

6. *Explosives with a low nitroglycerine content*. Here the main object of the nitroglycerine is to increase the sensitiveness to detonation and to ensure propagation of explosion. These are further divided into:

(a) Explosives for rock, containing ammonium nitrate, chlorates or perchlorates as the main explosives, with about 4 per cent of nitroglycerine.

(b) Permissible explosives with oxidizing salts as the basis, and 4 to 12 per cent nitroglycerine. These are powdery or so-called semi-plastic explosives.

CHAPTER XIX

POWDERY DYNAMITES

DYNAMITES WITH A CHEMICALLY INACTIVE BASE

Guhr dynamite

Kieselguhr dynamite was the first nitroglycerine explosive and was the first step in the development of the industry of the brisant explosives. It received its name from Alfred Nobel, who discovered the high absorbency of kieselguhr for nitroglycerine in 1866 and so provided the generic name for most of the high strength dynamites still in use today.

On the European Continent it is usually called dynamite No. 1, and in America giant powder No. 1.¹ Except for slight variations it contains 75 parts of nitroglycerine, absorbed in 25 parts of kieselguhr, per 100 parts of dynamite.

Although it develops a small amount of energy in comparison to its high nitroglycerine content, being inferior in this respect to gelatine dynamites of lower nitroglycerine content, and has therefore for a long time not been considered in Germany a rational explosive and has not been used for many years, nevertheless it is still asked for and exported to several countries. The ready displacement of the nitroglycerine from the kieselguhr by water makes it less suited to wet climates and wet boreholes. On the other hand, in hot climates such as Northern Chile, Asia Minor, etc., it has been used up until recent times. Perhaps its complete physical permanence even on long transportation and long storage in hot zones has been the reason for this, whereas with the colloided gelatine dynamites a reduction in sensitiveness has frequently been observed under the same conditions, regarding which more will be said at the proper place.

Kieselguhr. The first kieselguhr used in dynamite plants was discovered in the Lüneburg fields in the Province of Hannover, and was characterized by its exceptional purity. Kieselguhr also occurs

in many other places, as in North America, Scotland, France, Italy, and in considerable quantities in Norway.

It consists almost entirely of shells of diatoms, hence the name of infusorial earth, and can absorb and firmly retain liquids by capillary action of the tube-like structure. Its color varies from pure white to gray and yellow-green. The color is mostly due to iron oxide, and on roasting changes to a rose-red or dull orange color, but with many varieties the color remains almost white or dull red.

Since silicic acid, in addition to the above-mentioned impurities, forms the major portion of kieselguhr, mainly in the hydrated form, it is first subjected to a gentle roasting in a reverberatory furnace or muffle to remove the excess moisture and organic impurities before use in dynamite.

TABLE 21
Analyses of air-dried and anhydrous, calcined guhr

	GUHR NO. I (AIR DRIED)	GUHR NO. II (ROASTED)
	per cent	per cent
SiO ₂	94.3	96.34
MgCO ₃	2.1	—
Al ₂ O ₃	—	1.50
Fe ₂ O ₃ and Al ₂ O ₃	1.3	—
Fe ₂ O ₃	—	0.50
Organic material.....	0.4	—
CaO.....	—	1.64
H ₂ O.....	1.9	—

For dynamite only the finest grade, roasted, so-called white levigated kieselguhr, free from sand, is used, because particles of sand cause dangerous friction in the machine packing of dynamite cartridges.

After roasting, which should not be done at too high temperatures, since otherwise it will become "dead burned" and its absorbency suffer, and cooling, the lumpy guhr is put into roller mills where it is reduced to a fine powder. It is then passed through a shaker screen, packed into tight sacks and used immediately, so that it will not again absorb moisture.²

² See Guttman, *Die Industrie der Explosivstoffe* (1895), p. 101, for further details on the preparation of kieselguhr.

¹ Although the translator entered the explosive industry in 1911 he has never yet seen any guhr dynamite in the United States.

Escales³ gives two analyses (see table 21), one for air-dried (according to Sanford) and another for anhydrous, calcined guhr (according to Hagen). The guhr should not contain aluminium sulphate, because this can affect the stability of the dynamite unfavorably. In order to render the color of the dynamite independent of the kind of guhr and the roasting process of a few per cent of burned ochre or caput mortuum are added to it.

Manufacture of guhr dynamite. The mixing of the nitroglycerine with the kieselguhr is done in large wooden troughs or boxes about as high as a table, occasionally lined with sheet lead. It is given a preliminary mixing by wooden shovels or by hand, and the mass, consisting of coarse lumps, moist and dry particles, etc., is rubbed by hand through a coarse screen of about $1\frac{1}{2}$ meshes per centimeter into a second box. The screen consists of a wooden frame whose bottom is covered with a brass wire screen. The moist lumps are thus broken up and mixed with the dry particles. The rather uniform appearing mass is then turned over by shovels and put through a somewhat finer screen having about 3 meshes per centimeter into the first box. This second screening gives it the required fine subdivision and complete homogeneity.

The finished mix should be loose and crumbly, like fresh earth from the garden. It should appear neither too wet nor too dry, and should allow no nitroglycerine to be recognized. In no case should it appear distinctly moist. Its proper appearance is a matter of experience and practice. If it is too dry it is difficult to press into the cartridges because not slippery enough. If it is too moist the dynamite greases everything and shows a tendency to leak nitroglycerine and wet the cartridge paper, because the pressure of cartridging presses the oil out of the capillaries of the diatomaceous earth.

Since the absorbency of the guhr is not always uniform but varies, and good guhr generally gives a too dry dynamite when used in the proportion of 25:75, the properties are regulated by adding a poorer absorbent or a non-absorbent to maintain the nitroglycerine content uniform at 75 per cent. Such additions are heavy spar or talc, powdered chalk or magnesium carbonate, the latter also being able to neutralize any traces of acidity which may have formed. A small amount of calcined soda or sodium bicarbonate is often added for the same purpose.

³ Escales, *Nitroglycerin und Dynamit* (1908), p. 197.

Cartridging the dynamite. The use of loose masses of dynamite in mining should be prohibited by law everywhere. For loading boreholes the dynamite comes in the form of short, cylindrical cartridges 10 to 12 cm. long and 20 to 30 mm. in diameter. Diameters of 23 and 25 mm. are usual for the high strength nitroglycerine explosives. The cartridges are wrapped in parchment or paraffined paper, usually made in the dynamite plants by passing paper from an endless roll through a bath of molten, soft paraffin or a mixture of paraffin, rosin and talc. After cooling the paper should be coated with a rather hard but flexible film of 20 parts paraffin, 60 parts rosin⁴ and 30 parts

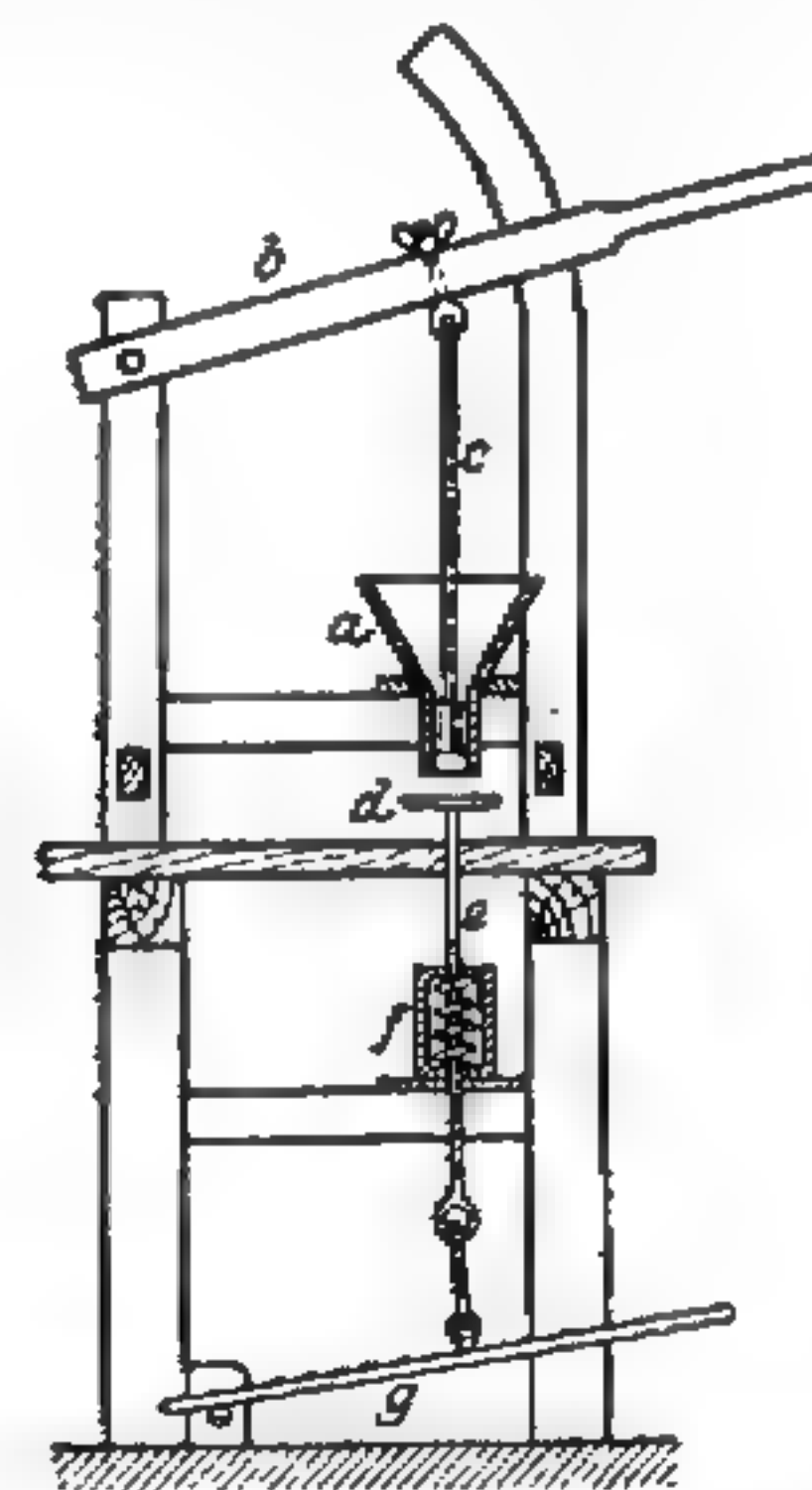


FIG. 25. CARTRIDGE PACKING MACHINE

talc. Paraffined paper forms a better protection against moisture than the more expensive parchment, and today is used almost everywhere.

In Germany red paper is prescribed for all explosives to be used in rock, to differentiate them from permissible explosives, the latter being in white or gray paper. Either intermittent or continuous cartridging machines, as described by Guttman⁵ are used. In the former the entire cartridge is pressed at one time into the prepared

⁴ Guttman, *Die Industrie der Explosivstoffe*, p. 487, figure.

⁵ Guttman, *Die Industrie der Explosivstoffe*, p. 482.

shell, while with the latter a continuous strand is formed, which from time to time is broken off into the desired lengths and wrapped in paper. This assumes a plastic condition of the mass. For dry, powdery dynamite or explosive mixtures only the intermittent method can be considered. Figure 25 represents a cartridge press which is much used.

Another intermittent press much used in many German plants is that shown in figure 26. It can be immediately understood from the drawing. Here the cartridge meets no pressure, the operator merely

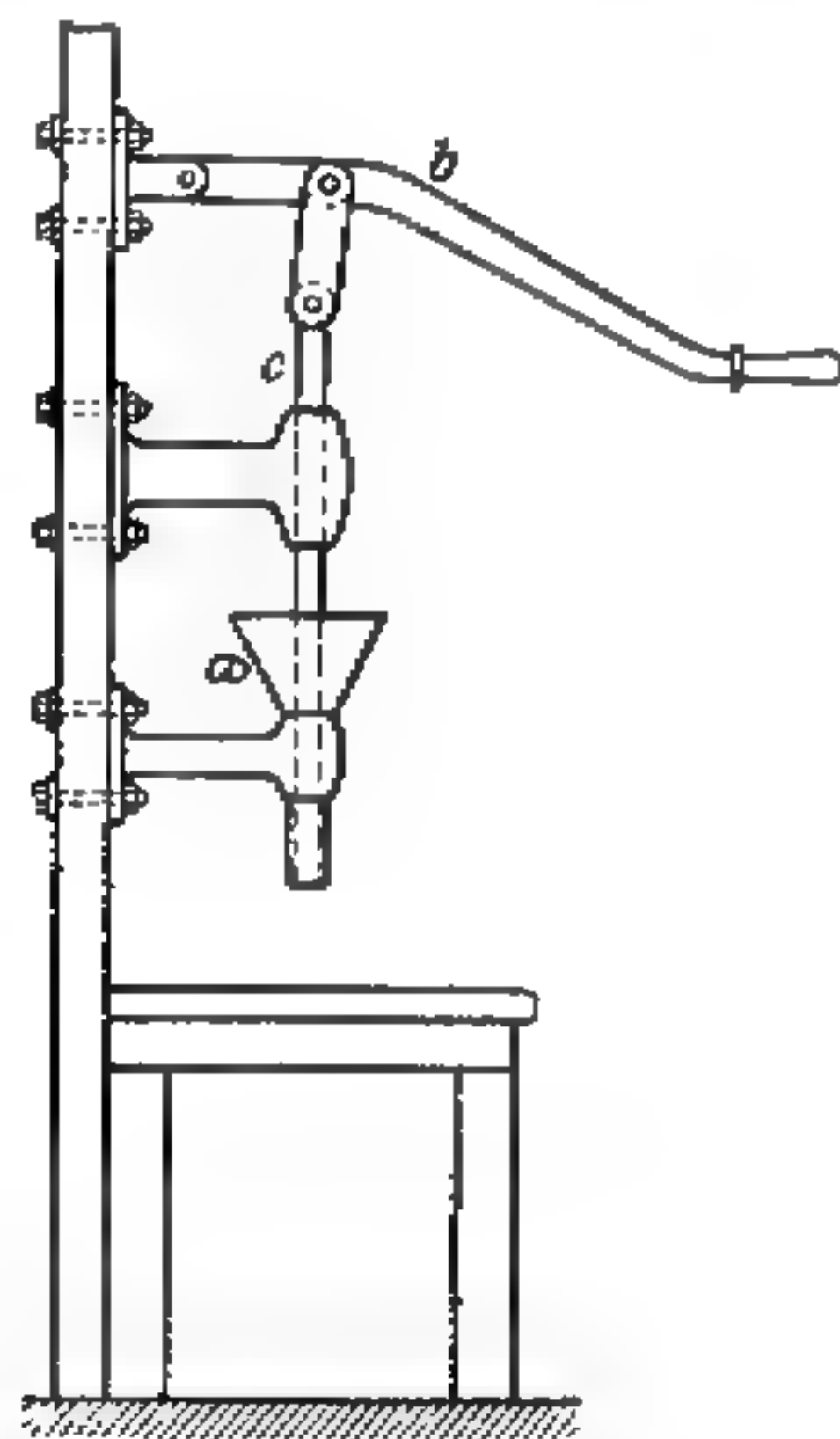


FIG. 26. CARTRIDGE PACKING MACHINE

holding the shell in his hand and the whole charge is pressed in at once, whereupon the cartridge is folded over by hand at the top. Particular value is placed upon neatly made, well closed folds. Instead of the metal funnel a linen bag is often used, and washed out from time to time or else renewed.

Guttmann describes a continuous cartridging machine which he himself built.⁶ (Fig. 27.) Guttmann recommends this press for rapid work and safety, since at each motion of the lever the pressure exerted is always smaller than in the case of intermittent presses.

⁶ *Industrie der Explosivstoffe*, p. 484.

In the United States of North American most of the presses used for loose dynamite (not gelatine) are automatic, pneumatic⁷ cartridging machines wholly constructed of wood.⁸ They consist of a rotatory member having four leaves or so-called shuttles, each shuttle holding 24 shells.⁹ The empty cartridge shells are placed¹⁰ upon the horizontal shuttles, the latter is then rotated to a vertical position by a quarter turn, and the dynamite packed in from a funnel above. On another quarter turn the filled and crimped cartridges are brought to a horizontal position. They are then picked up and packed into

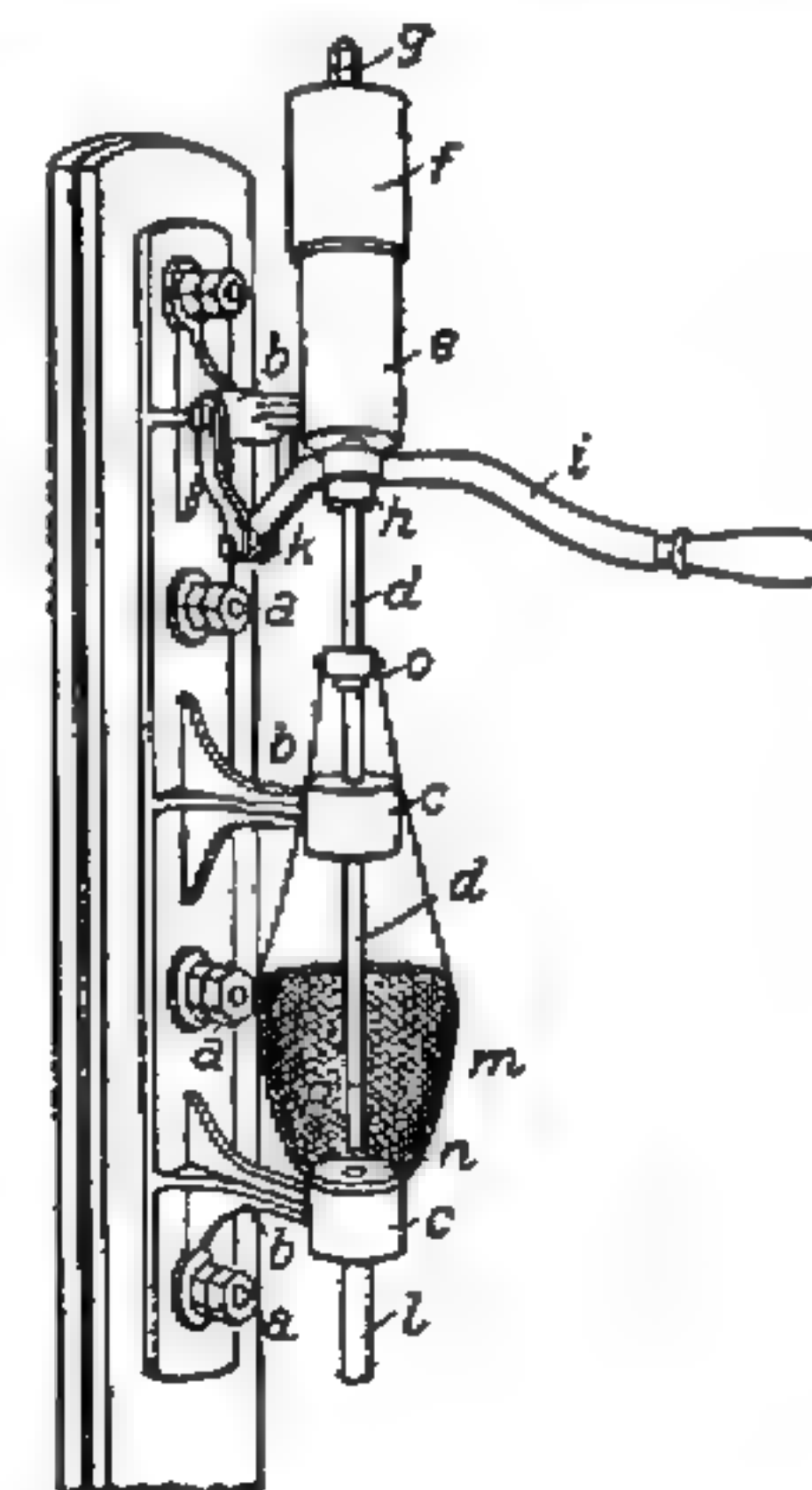


FIG. 27. CARTRIDGE PACKING MACHINE

boxes. With the help of this machine two operators can turn out relatively enormous quantities of packed powder, greater than is usual in Europe.¹¹

⁷ An error. They are mechanically driven.—TRANSLATOR.

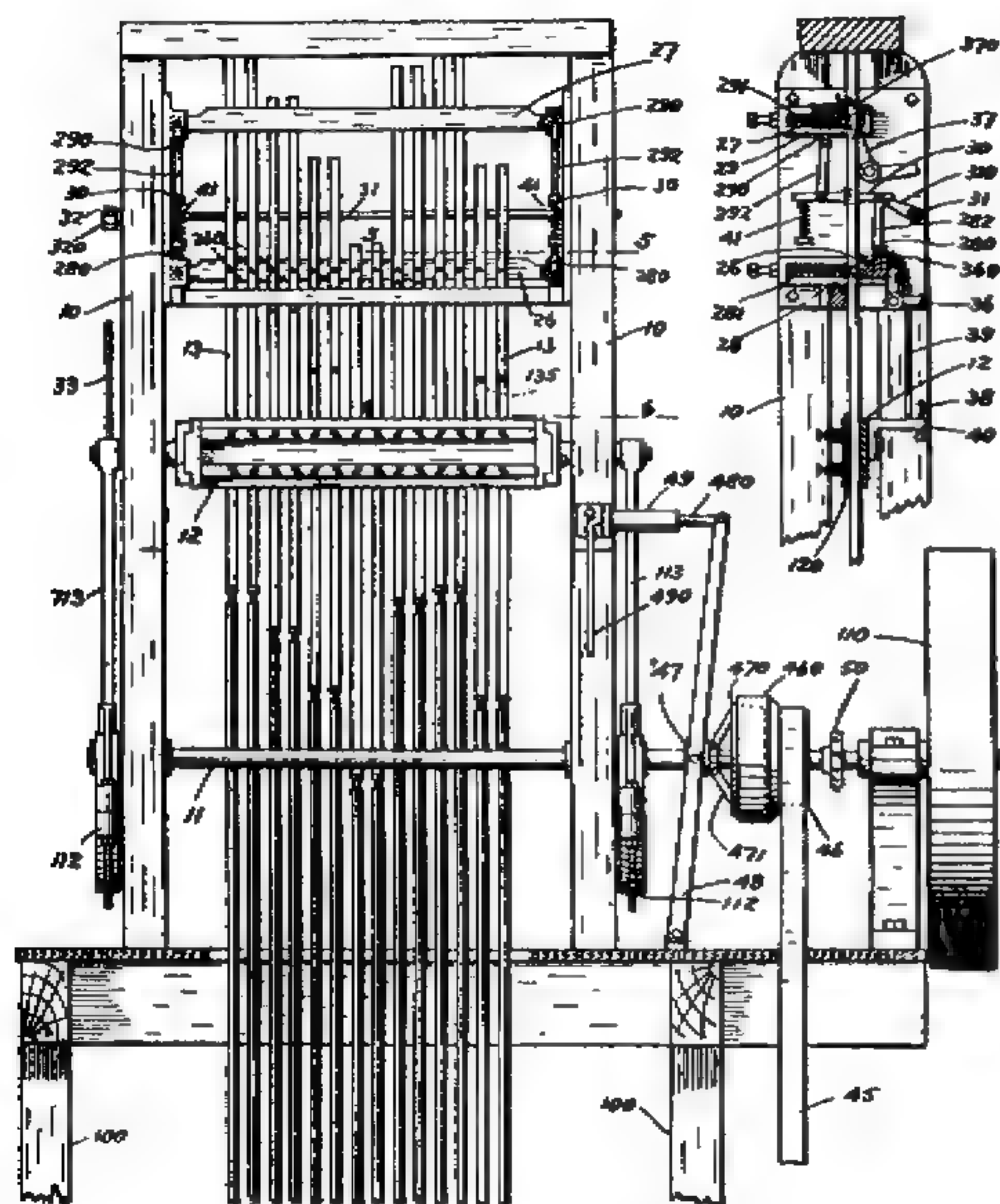
⁸ Not entirely of wood, but as far as practical to do so.—TRANSLATOR.

⁹ Each shuttle holds either 25 or 30 empty shells.—TRANSLATOR.

¹⁰ Placed mechanically.—TRANSLATOR.

¹¹ With the so-called "Hall Machines" an output per day of 40,000 pounds (18,000 kg.) of 1½ x 8 inch (31.75 mm. x 20 cm.) cartridges with two operators is not unusual. See United States patent 899592.—TRANSLATOR.

Moreover, in recent times machines have been constructed which automatically produce cartridge shells in great quantities. Such shell machines, which are complicated and expensive, can only be considered for large plants and large outputs.¹²



DYNAMITE CARTRIDGING MACHINE

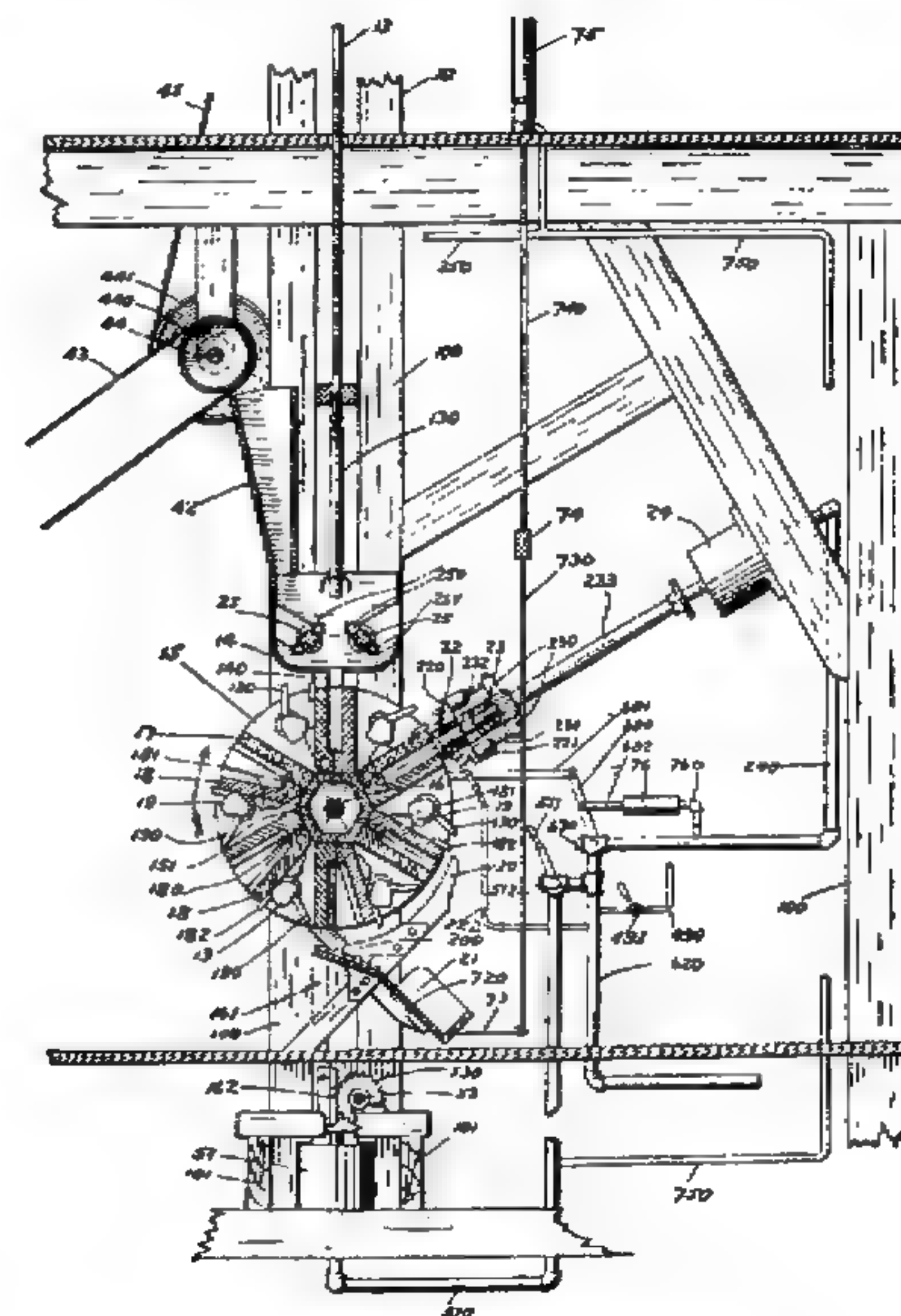
United States patent 899592

The cartridge paper cut by special cutting machines is in the form of an oblique rectangle, about 3 cm. shorter on one side than on the other. This gives a better closure of the cartridge.

Packing of the dynamite. Two and one-half kilograms of dynamite cartridges (in England 5 pounds) are packed in a pasteboard

¹² See diagram of Ayer Shell Machine, page 272.

carton and retained in position by corrugated paper to prevent shaking. Up to the time of the World War this was a requirement in Germany. The rectangular pasteboard cartons are usually made right at the plant by cutting and stitching, and are closed by a

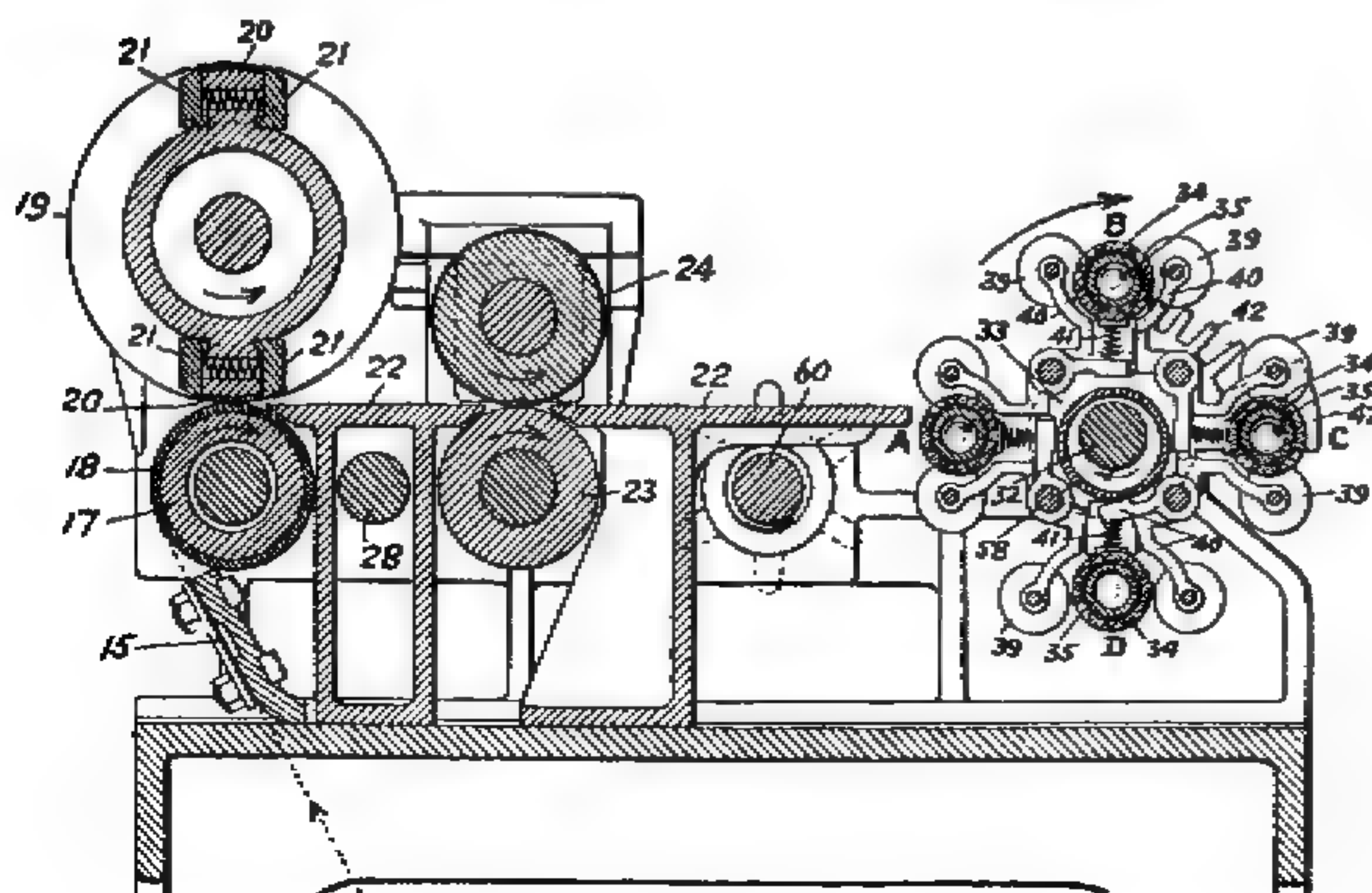
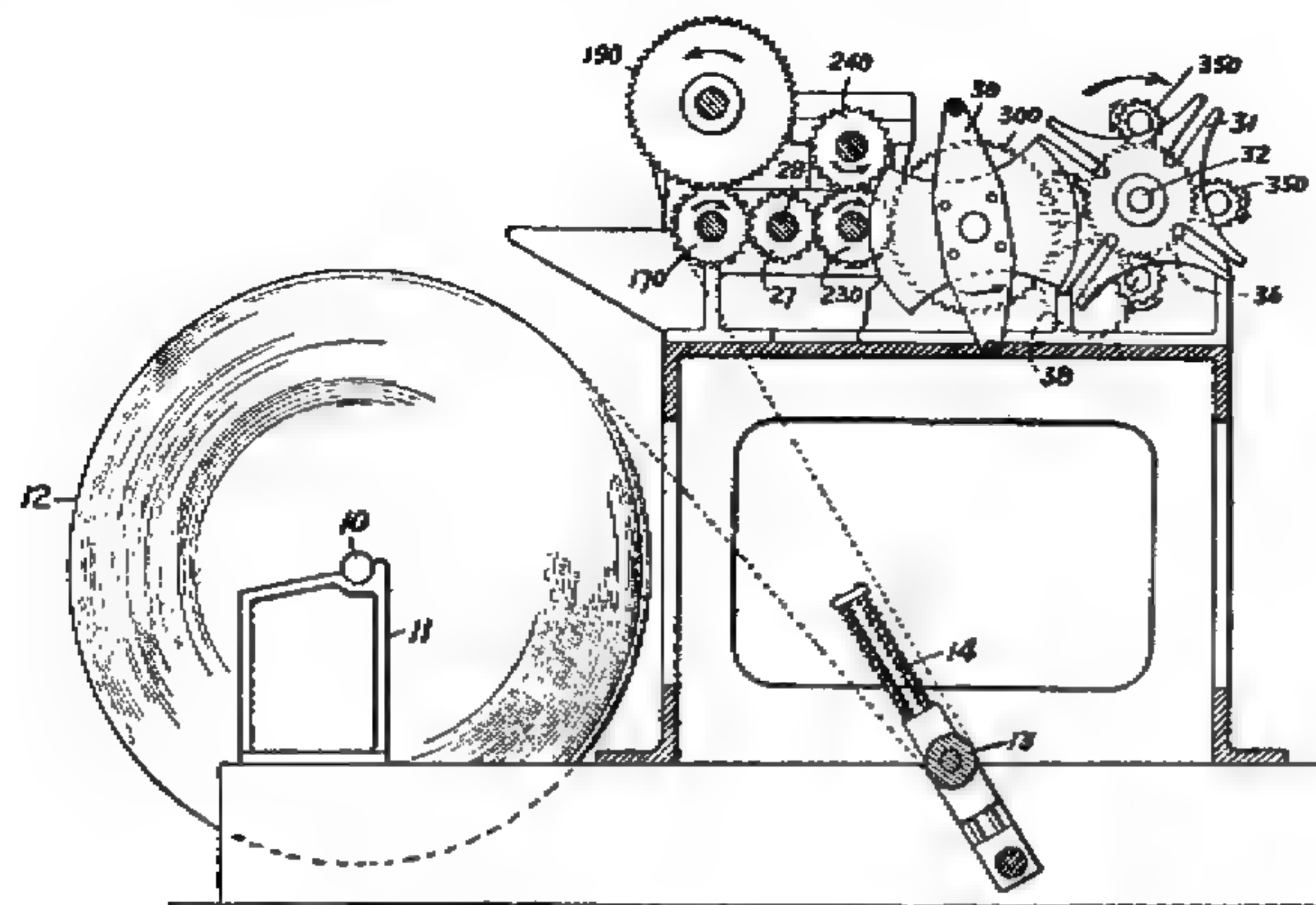


DYNAMITE CARTRIDGING MACHINE

United States patent 899592

suitable cover. Often they have a shape such that on folding together the flap forms the cover.

The cartons are wrapped in water-proof or ordinary paper and tied with string. In Prussia red wrapping paper is prescribed for cartridge paper for dynamite packing and for all non-permissible explosives, in order to differentiate from the permissible explosives, which are packed in gray paper.



MACHINE FOR MAKING PAPER SHELLS

United States patent 1575894

If the dynamites contain hygroscopic salts, particularly ammonium nitrate, ordinary, rather porous paper is used and the whole carton quickly dipped into a hot paraffin bath by means of a lever and cage, the temperature of the bath being about 80°C ., so that it is thickly covered and well protected against moisture.

Ten of such cartons, or 25 kg., are placed in a wooden box,¹³ whose size corresponds exactly to the size of the cartons. The boxes should not have iron bands around them, and as a rule do not have iron nails.¹⁴ Wood, brass, zinc or galvanized nails are used. Up until the World War the German railroad regulations prescribed projecting ears or reliable handles on the front of the box.

Chemical and physical properties of guhr dynamite

The chemical properties of guhr dynamite, like other mechanical mixtures of explosives, are governed by those of the constituents. The identification of guhr dynamite is very simple. A sample is digested with dry, pure ether, filtered from the kieselguhr, and the ether allowed to evaporate in a warm place at 30 to 40°C . If a drop of the oil remaining is taken up on blotting paper, placed on an anvil and struck with a hammer the resulting detonation shows the presence of nitroglycerine. Also the determination of the specific gravity (1.60) and the nitrogen content by the Lunge nitrometer (18.40 to 18.50 per cent) identify the nitroglycerine. If a drop of nitroglycerine is dissolved in concentrated sulphuric acid, and shaken with a dilute solution of potassium iodide-starch paste to which zinc shavings and dilute sulphuric acid have been added, a blue color is formed. If a few drops of nitroglycerine are dissolved in concentrated sulphuric acid, the solution poured into an excess of water, and a few drops of this put on the surface of a solution of some diphenylamine in concentrated sulphuric acid a deep blue color is formed. These reactions naturally are also produced by other nitric esters, such as nitroglycol, dinitrochlorohydrine.

The quantitative analysis will be considered at the end of this section.

Physical properties. Kieselguhr dynamite is a reddish-yellow, or if colored with ochre, a deep reddish-brown, odorless, crumbly-plastic mass, having a consistency somewhat similar to fresh earth.

¹³ Cartons are seldom used in the United States.—TRANSLATOR.

¹⁴ Only galvanized iron nails are used in the United States.—TRANSLATOR.

Guhr dynamite is not hygroscopic and attracts no moisture from moist air. On direct contact with water it has the property of allowing the nitroglycerine in it to be displaced by the water, separating the former in a liquid form. This process goes on slowly but surely, so that the penetration of water is a source of danger and wet dynamite is dangerous, since in wet boreholes the exuded nitroglycerine can under certain conditions escape into fissures and not be detonated by the explosion of the charge. On cleaning up with the pick, or on additional drilling in the vicinity, such nitroglycerine can be exploded mechanically and cause accidents.

Herein lies the fundamental physical difference between guhr dynamite and other loose dynamites on the one hand, and the gelatinous dynamites on the other hand. Nitroglycerine is converted into a kind of a solid state by collodion nitrocotton, also called merely collodion cotton, from which it cannot be displaced by water even by long contact.

Guhr dynamite shares the other physical properties of nitroglycerine, and naturally has a physiological action causing headache and being poisonous. Dynamite freezes at temperatures below 10°C., particularly readily at moderate winter temperatures, and the cartridges then form masses almost as hard as stone. The frozen dynamite is almost white. Often freezing occurs only after a long time, sometimes after a short time or after a few days, but always on long transportation in winter or during storage in winter in unheated buildings.¹⁵

For this reason with storage above ground in Germany there is probability of freezing for six months of the year. Guhr dynamite is much easier to freeze when in small quantities than is liquid or gelatinized nitroglycerine. Blasting gelatine seems to freeze the slowest.

Dynamite when once frozen thaws only very slowly because of its poor heat conductivity. For this reason the individual cartridges must be carefully thawed in kettles containing warm water. These consist of double walled, galvanized iron vessels filled with warm water at a maximum temperature of 70°C. The exterior and cover are protected from too rapid cooling by insulating material.

Volatility in the heat. On account of the low volatility of nitroglycerine any evaporation of it from dynamite under ordinary

conditions as from cartridge or packed dynamite, need not be taken into consideration, even at elevated temperatures. On the other hand, if it is spread out loosely the fine distribution and the increased surface exposed favor the volatilization of the nitroglycerine appreciably. At 40°C. a considerable amount volatilizes, even in a few days. At 70°C., when in a thin layer on a watch glass, all the nitroglycerine is lost by evaporation from dynamite after 100 hours, according to Hess.

Explosive character

Stability and stability tests. If guhr dynamite is made from fully stabilized nitroglycerine the dynamite is entirely stable, and can be stored an unlimited time, even in tropical climates, without any chemical change.

In the so-called Abel heat test with potassium iodide-starch papers, on the other hand, dynamite behaves differently and shows the reaction in a much shorter time than the nitroglycerine from which it is made. This is due to the greater surface of the nitroglycerine when in the form of loose dynamite, and the consequently increased vaporization. Apparently it is the vapor of nitroglycerine which dissociates at the temperature in question and colors the test paper.

This is supported by the fact that nitric esters of higher volatility than nitroglycerine, such as nitrolycol and trimethylene glycol dinitrate, in spite of their greater chemical stability on hot storage at 75°C., color the test paper in a much shorter time than nitroglycerine.

For this reason the dynamite itself is not tested, but the nitroglycerine is first separated by water and then subjected to the previously described Abel heat test. According to English regulations it must withstand this at least fifteen minutes at 71°C. (160°F.)¹⁶

For the investigation of a large number of daily samples in a works laboratory Oscar Hagen gives the following directions for displacing the nitroglycerine and making the test.¹⁷

"As many test tubes, each with a funnel placed on it, are arranged on a test tube rack as there are dynamite samples to be tested. The test tubes are 14 to 15 cm. high and 16 mm. in diameter. Each has a conical cork stopper, the

¹⁵ Regarding freezing see Escales, *Nitroglycerin und Dynamit*, p. 211.

¹⁶ Escales, *Nitroglycerin und Dynamit*, p. 206; Guttman, *Industrie der Explosivstoffe*, p. 651.

¹⁷ Report, *Analyt. Chem.*, p. 1 (1886); Escales, p. 207.

upper, smooth surface being marked to distinguish the samples. The funnels have a total length of about 8 cm., a neck about 1.5 cm. long and 3 mm. wide, and are about 17 to 18 mm. wide. The neck is loosely closed by a wad of pure blotting paper the size of a pea. The dynamite cartridges are thawed if frozen, and cut as finely as possible, one after the other, by a sharp, wooden spatula on a glass plate, crushed, and each funnel filled with the pulverized mass from one cartridge. Packing the dynamite in the funnel requires some practice. If compressed too much the tube is closed up and penetration of the water prevented. If compressed too lightly water and nitroglycerine run through together into the test tubes beneath, and new samples must be prepared. After all the funnels have been filled to four-fifths of their capacity in this way they are then filled up to the rim with distilled water at 90°C. The hot water causes a much faster filtration than cold water. The penetration of the water layer can be readily observed in the light colored dynamite, since it forms a sharply defined zone. When about 2 cc. of clear, water-free nitroglycerine has collected in the test tube the funnel is removed. With proper manipulation filtration of all the samples should be completed in thirty to forty minutes. The papers are then hung, the stoppers placed in position, and the tubes placed in the water bath. The cartridges are numbered, likewise the corks of the test tubes. With a well washed nitroglycerine the ensuing heating to 80°C. causes no discoloring of the paper after the lapse of an hour. The reaction, if any, appears first at the line between the moist and dry portions of the paper. In the presence of traces of acid this is shown as a light brown line, which on longer action of the acid vapors or with greater amounts of acid becomes wider and a deeper brown, finally passing into a blue."

Sensitiveness to shock and friction. Guhr dynamite is not quite as sensitive as liquid nitroglycerine to shock between hard metallic surfaces, but it nevertheless detonates easily between iron and iron or even between iron and other metals. Blows of wood on wood are ineffective. In the falling weight test with a 1 kg. weight a height of 12 to 15 cm., and with a 2 kg. weight a height of only 7 cm. is sufficient for detonation, according to Will. Frozen dynamite is less sensitive, and with a 1 kg. weight requires a fall of more than 1 meter, and with a 2 kg. weight at least 20 cm. Also friction between hard, rough surfaces easily causes detonation. However, the sensitiveness to concussion is not very high, since dynamite, particularly when in cartridges or in whole boxes, withstands very rough handling. The plastic mass is soft enough to be able to absorb even a considerable shock or blow without exploding. Whole dynamite boxes have been thrown off quarries 30 to 40 meters high without any more damage than breaking the boxes and partly crushing the dynamite to a pulp.

Firing into dynamite cartridges placed on a wooden support by a rifle only a short distance away causes an explosion every time, according to Guttman up to a distance of 60 paces, the velocity of the projectile naturally having some influence. Frozen dynamite in such a case is also much more insensitive and can be detonated only at short distances from the rifle.

Ignition. Small quantities of loose dynamite burn quietly when in contact with a flame or a spark. A fuse has even been put into a whole box of dynamite and lighted. The gases burst off the cover and the contents burned without explosion. However, this is an experiment which cannot be repeated with any guarantee of harmless results. If large quantities of dynamite catch fire the propagation of heat to adjacent particles increases to such an extent that the possibility of an immediate explosion must be taken into consideration. Explosion also occurs if the burning dynamite is enclosed in a metal or other container. If a dynamite cartridge is placed on a heated plate explosion within a short time can be counted a certainty.

Deflagration point. If a small quantity (0.1 to 0.2 grams) of dynamite is heated in a beaker on a bath of molten metal deflagration occurs above 180°C. on gradual heating, but in the ordinary method of making the test, at 20°C. rise per minute, deflagration occurs at 195 to 200°C. with a sharp report¹⁸ after first yellow, then red vapors have been emitted at about 175°C.

Detonation by initial impulse. Complete detonation is caused by even a weak initial impulse, i.e., by the weakest of the ordinary blasting caps, a No. 1. Guhr dynamite, like all mixed dynamites having a liquid ungelatinized nitroglycerine, is highly sensitive to an initial impulse.

Velocity of detonation. The velocity of detonation of guhr dynamite is of a very high order, varying with the density and diameter, but it does not attain the highest value obtained under the most favorable conditions with liquid nitroglycerine or blasting gelatine. Bichel gives 6800 meters per second,¹⁹ Kast 6650 meters at a maximum practical density of 1.50.²⁰ At lower densities of loading (1.30) in an iron pipe 34 mm. internal diameter the author found 5650 meters per second. Guhr dynamite made from nitroglycol gave 6000 meters per second under the same conditions.

¹⁸ Kast, *Spreng- und Zündstoffe*, p. 22.

¹⁹ *Untersuchungsmethoden für Sprengstoffe*, Berlin, W. Ernst & Sohn, 1902.

²⁰ Kast, *Spreng- und Zündstoffe*, p. 70 (1921).

Energy content. The energy content as measured in the calorimetric bomb (or heat of explosion) naturally amounted to three-fourths of that of nitroglycerine, since the chemically inactive absorbent does not take part in the decomposition, or about 1200 Calories per kilogram with water as a liquid. Escales found 1170 Calories, and Kast 1090 Calories with water as a vapor.

The gases of explosion of all dynamites having chemically inactive absorbents are the same as those from nitroglycerine. One kilogram of guhr dynamite gives 536 liters of gas on explosion.

Explosive strength and brisance. Dynamites with an inactive absorbent are naturally less brisant than liquid nitroglycerine and give a lower effect than the quantity of nitroglycerine present would be expected to give when compared with the effect produced by liquid nitroglycerine or blasting gelatine. The heat developed is distributed to the decomposition products and the indifferent absorbent material, which at constant volume has about the same specific heat (0.19) as the gaseous decomposition products of the nitroglycerine.

Naturally the temperature of explosion is also lower than that of nitroglycerine. According to Escales it goes up to about 3000°C. According to Brunswig it is 3160°C., to Kast 3420°C. For nitroglycerine Escales calculated from the Heise data 3160°C., and from the Brunswig data 3470°C. Kast found the much higher figure of 4250°C.

The inert admixture on the one hand hinders the passage of the wave of detonation, and does not permit the maximum velocity of detonation which is reached under favorable conditions by nitroglycerine, but on the other hand the pulverent condition and the enclosed air favors the passage of the wave of detonation, as was brought out in the consideration of the ease of explosion of the various liquid nitric esters, so that the initial velocity of guhr dynamite is higher, and such a low velocity as is attained under certain conditions with liquid nitroglycerine, as with small diameters and slight confinement, is never found with guhr dynamite.

Lead block expansion. According to the above a lower lead block expansion would be expected than that corresponding to the quantity of nitroglycerine present, as compared to the expansion given by liquid nitroglycerine. Ten grams of liquid nitroglycerine under sand tamping give a net expansion of 550 cc. Ten grams of 75 per

cent guhr dynamite under sand tamping give a net expansion of 320 cc. By a proportion the 7.5 grams of nitroglycerine present would lead one to expect 410 cc. without the damping effect of the inert ballast, but it should be remembered that the lead block figures do not increase exactly proportionately to the quantities used, but in a geometrical proportion, particularly at high values.

Under water tamping, which gives higher values, the comparative lead block expansions were obtained which are given in table 22. The explosive effect per unit weight of nitroglycerine is therefore reduced 14 to 18 per cent by the inert, heat-absorbing absorbent.

Propagation of detonation. Guhr dynamite shows strikingly the property of simultaneous explosion of separated cartridges when only one is detonated (intentionally). The test of propagation of

TABLE 22
Comparative lead block expansions

10 GRAMS LIQUID NITROGLYCERINE	10 GRAMS NITROGLYCERINE MIXED WITH 3.4 GRAMS OF GUHR	7.5 GRAMS LIQUID NITROGLYCERINE	7.5 GRAMS NITROGLYCERINE MIXED WITH 2.5 GRAMS OF GUHR
630 cc.	540 cc.	450 cc.	370 cc.
Difference, 90 cc.		Difference, 80 cc.	

detonation over a space is one of the most characteristic and most important tests in the practical manufacture of most explosives.

The presence of liquid nitroglycerine, finely subdivided in the pulverent explosive mixture, always ensures reliable propagation of detonation unless the opposing effect takes place from too great an admixture of desensitizing materials.

Cartridges of guhr dynamite 30 mm. in diameter can propagate detonation over a space of 30 cm. between cartridges.

Blown-out or burned shots. With proper detonation of dynamite the gases formed on explosion, namely, carbon dioxide, nitrogen, water vapor and some oxygen, are not injurious to health or poisonous. On the other hand, in actual practice the charge occasionally burns slowly in the borehole, giving a so-called blown-out shot. In this case there is not complete decomposition of the nitroglycerine molecule. The nitric acid radical does not give off all of its oxygen of account of too low a temperature, and nitric oxides are formed,

the simple oxide, NO, forming the very poisonous nitrogen dioxide, NO₂, when in contact with the air. Moreover a further result of incomplete decomposition is the formation of poisonous carbon monoxide. In such a case a reddish-yellow vapor escapes from the borehole, which is injurious to the miner if inhaled. A typical case of this in actual practice has been described by Jacoby and His in two medical articles.²¹

The causes of blown-out shots may be as follows:²²

Too weak caps, such as those rendered unsuitable by moisture, firing by means of percussion caps alone without blasting caps, or improper placement of fuse and cap in the charge so that the explosive is ignited by the fuse before explosion of the blasting cap and partly burns before explosion due to the blasting cap. Also the use of frozen dynamite, or plugs of drillings between the various cartridges, can cause partial or complete blown-out shots. If the shot blows out at first the gas pressure formed subsequently in the borehole, with the rise in temperature resulting, can lead to explosion. In any case poisonous gases are formed. The proposed preventative formed of cartridges which give off oxygen (German patent 185363) cannot be wholly effective, and they are seldom used, because the corresponding increased cost can be better applied to furnishing perfect blasting caps and fuses. Properly placing and tamping the shot, after careful cleaning of the borehole from drillings, is also a most effective means of avoiding blown-out shots.

Frozen dynamite. In cold weather dynamite cartridges freeze to a hard, firm mass, as stated previously, into which the blasting cap cannot be forced, and which moreover cannot be detonated by mere cap initiation. On the other hand, by placing a charge of a brisant explosive on top of it it is possible to secure detonation. According to Guttman such a brisant explosive may be gun cotton saturated with nitroglycerine. Here there is a certain parallel with the case of detonation of other highly brisant explosives when in a similar, crystallized, hard condition. Thus highly compressed charges of other explosives, which in a pulverent state are easily detonated by a blasting cap, such as charges of compressed ammonal, a mixture of ammonium nitrate, aluminium powder and trinitrotoluene, or cast, crystallized trinitrotoluene-ammonium nitrate mixtures such as were

used to a great extent during the World War for filling brisant grenades, also cast charges of trinitrotoluene or picric acid, both of which detonate easily when in the form of a loose powder, require a stronger initial impulse to detonate them, or a so-called priming charge.

Such priming charges, used in artillery shells, which are in turn set off by a blasting cap, are not suitable for practical use because frozen cartridges lack the necessary plasticity and cannot be placed in the bottom of a borehole easily and without dangerous friction.

Frozen dynamite cartridges must therefore be carefully thawed, which is done in the warm water cans previously described (Nobel Cans²³). In no case should thawing be done over an open flame, near stoves or hearths, or by contact with hot objects such as steam pipes, etc. Countless accidents have been caused by careless thawing of dynamite cartridges. Statistics show that most of the accidents in using dynamite occur in the cold part of the year.

It is not always possible to prevent frozen cartridges being given the miners, because frequently the outside cartridges in a carton are soft while in the center they are still wholly or partly frozen. In mining operations explosives magazines are often below ground, where the temperature is sufficiently high at a suitable depth to prevent freezing, or to thaw dynamite frozen during transportation. Heating magazines above ground by hot water is expensive and not always possible. Thawing takes time, in spite of suitable apparatus, and is inconvenient.

For many uses of dynamite, such as road construction, driving tunnels, shafts by the freezing process, engineering work in the mountains, such as cutting water-ways, it is therefore best to have recourse to non-freezing types of dynamite in the colder parts of the year, or from October to April. Such dynamites are coming into use more and more.

In itself frozen dynamite is less sensitive to mechanical influences than a plastic dynamite, as would be expected from a theoretical consideration, and this has been confirmed by exact tests. On the other hand, according to the observations of Hess, dynamite in a half-frozen state, or in the transition stage, is more sensitive and

²¹ Z. Schiess- u. Sprengstoffw. (1907), p. 261.

²² Wappler, Jahrb. f. Berg- u. Hüttenw. im Königr. Sachsen (1887) p. 31.

²³ See Escales, *Nitroglycerin und Dynamit*, p. 215, "Dynamite Thermophores;" also *Österr. Z. f. Berg- u. Hüttenw.*, vol. 49, No. 17; and *Mitteil. Gegenst. Art. u. Geniewesen* (1901), No. 10.

dangerous. With the slight friction involved this circumstance is not easily understood, and the author has frequently crushed by a wooden hammer blocks of nitroglycerine frozen in a test tube together with glass, or frozen cartridges, with suitable protection for himself, without causing an explosion. In carrying out such a test great precautions are advised, however.

DYNAMITES WITH A CHEMICALLY ACTIVE BASE

The oldest process of allowing nitroglycerine to be absorbed by a combustible or explosive substance, is due to Nobel himself, who filled sheet zinc shells with black powder and poured in nitroglycerine to saturate it. The shells were closed by a cork stopper.²⁴

Gun cotton dynamite, proposed about 1867 by both Trauzl and Abel, is in the class of the oldest dynamites having an active base. Trauzl's dynamite consisted of 73 per cent nitroglycerine, 25 per cent gun cotton and 2 per cent charcoal, and was sold in a moist state, containing about 15 per cent of water. In this condition it detonated with a strong blasting cap and propagated detonation well. Its products of explosion naturally contained carbon monoxide. Abel saturated a mixture of potassium nitrate and gun cotton with nitroglycerine and called the product "Glyoxilin."

Schultze in 1868 proposed a mixture of wood nitrocellulose and nitroglycerine, called "Dualin."

Under the same name Dittmar patented a mixture of 50 per cent nitroglycerine, 30 per cent nitrated sawdust and 20 per cent saltpeter.

The gun cotton dynamites had a highly brisant effect, but naturally a low density. With the discovery of gelatine dynamites they were soon almost completely abandoned.

The mixed dynamites (called simply dynamite in the United States) in which the nitroglycerine was absorbed in a mixture of wood meal, or occasionally charcoal in part, and saltpeter instead of the incombustible kieselguhr, attained considerable importance, the proportions between saltpeter and combustible material being usually but not always so chosen that only carbon dioxide, nitrogen and water vapor were found in the gases of explosion, with no carbon monoxide, which naturally was of great importance in underground work.

²⁴ *Dingler's Polytechn. Journ.*, January 1, 1864.

Such dynamites, having a typical composition as follows:

	per cent
Nitroglycerine.....	40
Sodium nitrate.....	45
Wood meal.....	12
Carbonate and moisture.....	3
	<hr/> 100
Oxygen balance.....	+9.35

are much used in Austria, France and America, and up to the present time have been widely used in the United States under the name of "Straight Dynamites."

In European mining it can be said that they have been gradually replaced by gelatine dynamite, which is less sensitive to moisture and more dense.

German mining at present no longer knows any representatives of this type, and the Prussian police regulations of February 1, 1923, which embody regulations for explosives for Prussian mining, permit only gelatine dynamite.

Liquid nitroglycerine is used in Germany and England in the so-called semi-plastic permissible explosives to the extent of about 12 per cent of the mixture. At first kieselguhr was still added to ensure absorption.

The variations and the degrees of strength due to varying nitroglycerine content are innumerable, and only a few of the more important compositions given by Guttman and Escales will be given in table 23. French dynamite No. 0 is similar in composition to Atlas Powder, containing 74 per cent nitroglycerine and 26 per cent wood meal. Based upon anhydrous wood meal and the latter calculated as cellulose, it contains 28.6 per cent oxygen less than is required for complete combustion, and consequently on explosion gives considerable quantities of carbon monoxide and hydrogen. The lead block expansion amounts to about 410 cc. net, and the Hess lead block is crushed 19 mm., as with gelatine dynamite. The density is about 1.40.

Of the mixtures given in table 23 the one having the highest explosive strength is Rhexit, with an oxygen deficiency of only 11 per cent, a lead block expansion of 385 cc. net, a crushing effect of 20 mm., and a density of 1.54. The effect is therefore about the same as that of a gelatine dynamite of similar composition, but explosives of this kind

TABLE 23

Variations and degrees of strength of dynamite due to varying nitroglycerine content (after Guttman and Escales)

RHEXIT (ACCORDING TO DILLER)		MEGANIT	
	per cent		per cent
Nitroglycerine.....	64.0	Nitroglycerine.....	60.0
Wood mould.....	11.0	Nitrated wood pulp.....	10.0
Wood meal.....	7.0	Nitrated ivory nut meal.....	10.0
Sodium nitrate.....	18.0	Sodium nitrate.....	20.0
CARBONIT (ACCORDING TO SCHMIDT AND BICHEL)		STONIT (ACCORDING TO SCHMIDT AND BICHEL)	
	per cent		per cent
Nitroglycerine.....	25.0	Nitroglycerine.....	68.0
Wood meal.....	40.5	Kieselguhr.....	20.0
Sodium nitrate.....	34.0	Wood meal.....	4.0
Soda.....	0.5	Potassium nitrate.....	8.0
HERCULES POWDER (AMERICA)*		VULCAN POWDER (AMERICA)†	
	per cent		per cent
Nitroglycerine.....	40.0	Nitroglycerine.....	30.0
Sodium nitrate.....	45.0	Sodium nitrate.....	52.5
Wood pulp.....	11.0	Sulphur.....	7.0
Salt.....	1.0	Charcoal.....	10.5
Magnesium carbonate.....	1.0		
Moisture.....	2.0		
SAFETY NITRO POWDER (AMERICA)‡		ATLAS POWDER (AMERICA)‡	
	per cent		per cent
Nitroglycerine.....	69.0	Nitroglycerine.....	75.0
Sodium nitrate.....	18.0	Wood fiber.....	21.0
Wood pulp.....	13.0	Sodium nitrate.....	2.0
		Magnesium carbonate.....	2.0

* This composition is no longer sold under this name, although similar compositions having a better oxygen balance and less moisture are very widely used.

† This is no longer known in the United States.

‡ These are no longer known in the United States. For many years no dynamite except a gelatine dynamite has been allowed to contain more than 60 per cent nitroglycerine, on account of danger of exudation. —TRANSLATOR.

are very sensitive to moisture and in wet rock allow nitroglycerine to escape, which can give the troubles mentioned previously.

The cheapness and simplicity of manufacture should be noted, as it avoids the use of the always expensive collodion nitrocotton for conversion of nitroglycerine into the form of a gelatine. The nitroglycerine in its liquid but finely divided form ensures propagation of detonation and a highly brisant effect in such mixtures rich in nitroglycerine, and consequently high velocity of detonation, while desensitization, such as can occur in a too stiff gelatine, does not come into consideration.

TABLE 24

Compositions of French ammondynamites

	AMMONDYNAMIT		
	1	2	2a
	per cent	per cent	per cent
Nitroglycerine.....	40	20	22
Ammonium nitrate.....	45	75	75
Sodium nitrate.....	5	—	—
Wood or cereal meal.....	10	5	—
Charcoal.....	—	—	3
	100	100	100
Oxygen balance.....	+0.75%	+9.7%	+7.8%
Lead block expansion.....	400.00 cc.	335.0 cc.	330.0 cc.
Lead block crushing.....	22.00 mm.	15.5 mm.	16.0 mm.
Density.....	1.38	1.20	1.33

These dynamites are made in the same way as guhr dynamite, by simply mixing the nitroglycerine with the absorbent mixture. They are loose, moist, greasy powders which should allow no oil to exude on gentle pressure. Paraffined cartridge paper is used for the shell, which does not allow the nitroglycerine to exude. The pasteboard cartons holding the cartridges are wrapped in paper and dipped into a bath of hot, melted paraffine to protect them from moisture.

A particularly strong representative of this type was the so-called ammondynamite,²⁵ in which ammonium nitrate is used as the oxygen carrier instead of potassium or sodium nitrate, and on account of its

²⁵ Called "ammonia dynamite" in the United States.—TRANSLATOR.

entire decomposition into gases without leaving any solid residue it gives a particularly favorable gas pressure. Naturally all these mixtures, like all ammonium nitrate explosives, are particularly sensitive to moisture.

The French ammondynamites have the compositions shown in table 24.

In this connection there should be mentioned the rock explosive still much used in America called Monobel,²⁶ consisting of a mixture of 80 per cent ammonium nitrate, 10 per cent nitroglycerine and 10 per cent wood meal, having an oxygen balance of 4.35 per cent, a lead block expansion of about 350 cc., a lead block crushing effect of 12 mm. and a density of about 1.15. This explosive belongs to the class of typical ammonium nitrate explosives rather than the dynamites. With ammonium nitrate explosives the same effect is obtained even with low nitroglycerine contents. It therefore comes into consideration only in a country where nitroglycerine is a comparatively cheap product and the nitroglycerine content is of little importance for transportation requirements.

In Germany such explosives as Monobel or Ammondynamit No. 2 are not used because the specific effect of the nitroglycerine is no different from that also obtained from ammonium nitrate explosives containing only small quantities (4 per cent) or no nitroglycerine, and the latter have the advantage of absolute safety in handling and in being permitted on the railroads as packages without restriction.

²⁶ Monobels in the United States are permissible explosives for use in coal mines, and have some use in quarries.—TRANSLATOR.

CHAPTER XX

BLASTING GELATINE

An epoch-making advance over guhr dynamite and mixed dynamites, and a climax of all Nobel's inventions probably not yet outranked, was the discovery in 1875 of the gelatinizing of nitroglycerine by collodion cotton (soluble nitrocellulose), i.e., the preparation of a plastic, elastic colloid, a solid solution of nitrocellulose in nitroglycerine. The desired handy, solid form was thus obtained in a state of very high energy concentration, absolute stability and permanence in the presence of moisture, and of the most favorable chemical composition, since the mixture was the best from the physical and explosive point of view and at the same time had those proportions in which the oxygen excess of the nitroglycerine was balanced by the oxygen deficiency of the nitrocellulose, thus giving the highest chemical energy development by complete combustion and avoiding injurious products of explosion.

A gelatine composed of 8 parts enneanitrocellulose and 92 parts of nitroglycerine fulfills these conditions of complete combustion to carbon dioxide, water and nitrogen.

Nobel patented his discovery in almost all civilized countries.¹ The preface of the Swedish patent, which gives all the important points of the epoch-making discovery in a concise form, is shown here as a translation by Escales:

"As is well known, nitroglycerine in a liquid form has been found too dangerous for commercial use. On account of this danger I have invented dynamite, i.e., nitroglycerine absorbed in very porous materials. However, dynamite has only two-thirds the strength of nitroglycerine and is spoiled by contact with or under pressure of water, because the liquid nitroglycerine is in this way displaced from the dynamite. For this reason I have attempted to give the nitroglycerine a solid form in another way. I attain this object by a gelatinization process. This is done by dissolving in the nitroglycerine, gently heated on a water bath, nitrocellulose such as is used in the preparation of collodion. The explosive liquid thereby becomes more or less viscous, and

¹ German patent 4829, see also Introduction; British patent 4179 (1875); Swedish patent of July 8, 1876.

after it has absorbed 6 to 7 per cent of its weight of nitrated vegetable fiber it attains a rubbery or gelatinous consistency, particularly well suited for industrial purposes. However, I do not limit the solution to the above composition, because for various purposes various degrees of hardness of the explosive are required, and the degree of hardness depends upon the relative amount of dissolved, nitrated vegetable fibers. In the gelatinization of the nitroglycerine care should be taken that (1) this liquid contains no impurities which will prevent it from dissolving nitrated cellulose when warm and affecting it adversely, (2) that only readily soluble nitrocellulose is used, and (3) that solution of the nitrated cellulose, especially if the latter be matted together, is facilitated by working and kneading the mass.

"The gelatinized nitroglycerine can be easily pressed into cartridges or given other shapes."

The gelatinized nitroglycerine so obtained has the composition 90 to 93 per cent nitroglycerine and 7 to 10 per cent collodion cotton. It has been called "blasting gelatine," and is the strongest and most brisant of all practical explosives hitherto used, finding its main use in the toughest and most solid rock. It has also found use in the form of a thinner gelatine, poorer in collodion cotton, as the basis of an endless series of gelatinous, plastic explosives of very many graduated strengths and degrees of brisance, commonly called gelatine dynamites² but which have sometimes other names depending upon origin and particular characteristics. Their high density is quite general, as well as comparatively high insensitiveness to moisture and relatively high brisance, depending upon the nitroglycerine content. Moreover, explosives permitted in the presence of fire-damp and coal dust have been prepared on a gelatinized nitroglycerine basis, having a 25 to 50 per cent content of the latter, depending upon the requirements of brisance and degree of safety in fire-damp.

MANUFACTURE OF BLASTING GELATINE

Collodion cotton

Collodion cotton, the ether-alcohol soluble form of gun cotton, is not a uniform, chemical substance, but a mixture of various degrees of nitration of cellulose, usually the octa-, ennea- and decanitrocellulose:

	<i>per cent of nitrogen</i>
$C_{24}H_{12}O_{12}(ONO_2)_8$ with	11.11
$C_{24}H_{10}O_{11}(ONO_2)_9$ "	11.97
$C_{24}H_{10}O_{10}(ONO_2)_{10}$ "	12.75

² Called simply "gelatine" in the United States.—TRANSLATOR.

In general the range of collodion cotton is between 11.1 and 12.5 per cent nitrogen content.

According to Lunge³ nitrocellulose soluble in ether-alcohol is obtained by nitrating cotton with a mixture of equal parts of nitric and sulphuric acids containing 17 to 18 per cent of water, the solubility increasing with rising temperatures of nitration, while on the other hand the time of nitration must be limited at elevated temperatures. According to Guttman⁴ the customary nitrating mixture is 1 part of cotton to 25 to 30 parts of an acid mixture containing equal parts of 75 per cent monohydrate nitric acid, specific gravity 1.44, and 96 per cent monohydrate sulphuric acid, specific gravity 1.84. Such a mixture contains 37.5 per cent HNO_3 , 48 per cent H_2SO_4 and 14.5 per cent H_2O . Nitration takes one to one and a half hours at 40°C.

A part of the spent acid is removed, and a part is revived by an acid mixture high in nitric acid and low in water, i.e., brought back to the original composition. The amount of this revivifying mixture used depends upon the concentration of the acids available.

Nitration can be done in stone jugs, as in the manufacture of gun cotton, but it is usually done directly in nitrating centrifugals, in which the spent acid is separated immediately after nitration and displaced by water for the greatest possible recovery of the valuable nitric acid. Displacement can also be done first with sulphuric acid, followed by water. Neutralization, boiling and pulping in Hollanders, and stabilization are processes well known in the manufacture of gun cotton.

The governing factors are: (1) Concentration of the acid mixture, (2) Temperature of nitration, (3) Time of nitration.

High concentrations and long times have a tendency to form highly nitrated, slightly soluble nitrocellulose, while high temperatures give lower degrees of nitration. Regulation of these three factors makes it possible to obtain collodion cotton of the desired composition and solubility.

Specifications for collodion cotton. The following properties of collodion cotton are important in the manufacture of blasting gelatine and gelatine dynamite: chemical stability, solubility, viscosity,

³ *Z. angew. Chem.*, (1906) p. 2051.

⁴ *Industrie der Explosivstoffe*, p. 361; *Z. angew. Chem.* (1907), p. 262.

gelatinizing powers with nitroglycerine, combining power with nitroglycerine and nitrogen content.

Stability test. One gram of dry collodion cotton is subjected to the Abel test at 72°C. as described under Nitroglycerine Manufacture. The reaction should not occur within fifteen minutes. In England only ten minutes is allowed. In Prussia a period of twenty-five minutes at 80°C. is required for collodion cotton or gun cotton intended for the manufacture of smokeless powder. Well stabilized collodion cotton will usually withstand the test at 72°C. longer than thirty minutes.

A number of years ago it was customary in some factories to use very small quantities of corrosive sublimate in the manufacture of nitrocellulose. This was done because it has been observed that nitrocellulose in a moist state,

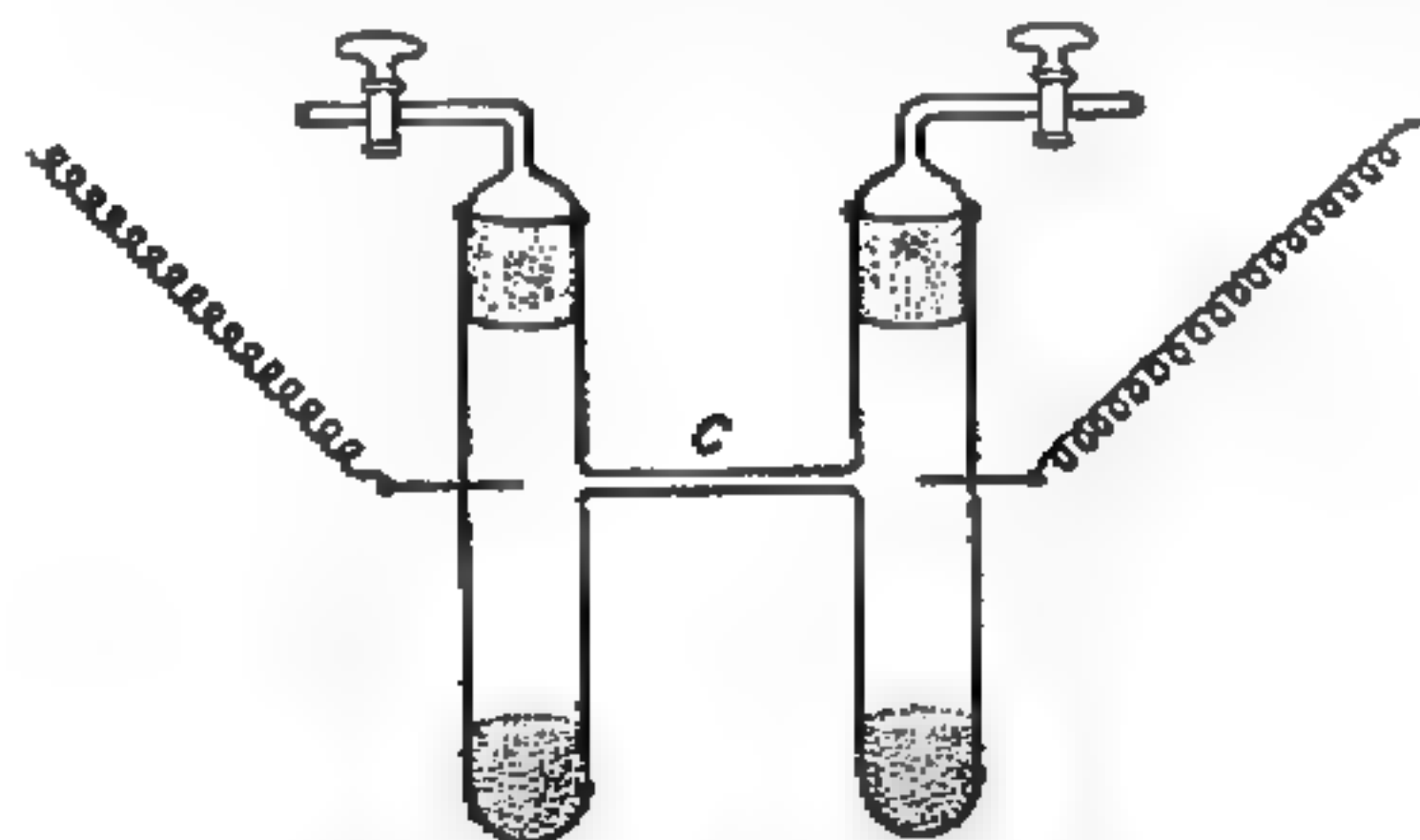


FIG. 28. SPECTROGRAPHIC DETERMINATION OF MERCURY IN EXPLOSIVES

as packed, stored and sold, was attacked by certain bacteria. The corrosive sublimate was said to prevent the activity of these bacteria, render the nitrocellulose antiseptic and prevent the formation of mould on the sacks. It was reduced to mercury by the fibers and present as such in the collodion cotton and the explosives made from it. The readily volatile mercury, even when present in small quantities, masked the test reaction, since it formed iodide of mercury with iodine separated from the test paper containing potassium iodide and starch, which iodide of mercury remained invisible in the small quantities corresponding to the sensitiveness of the iodine-starch reaction. Such added materials as mask the Abel test and render it useless are therefore forbidden by the authorities in countries where particular importance is placed upon this test, as in England and its colonies.

Even the slightest contamination of nitrocellulose by mercury can be recognized very simply by the spectroscope, by placing the sample in an evacuated tube having two legs joined together by a capillary tube, each leg having a platinum wire fused into it. The vessel is evacuated, heated in a water bath, the capillary (c) brought before a spectroscope and a spark from an induction coil passed through it, the presence of mercury making itself known by the mer-

cury spectrum, a yellow double line, a strong green line and two weak violet lines (fig. 28).

A still more delicate test which makes traces of mercury visible which could be shown in no other way, is by heating to drive out the mercury vapors and precipitating them on a pure gold plate, which has an enormous attraction for these vapors, drawing them out of the surrounding air. This contaminated gold sheet is then heated in the apparatus described above. The spectroscopic test, with the use of a large spectroscope, a good vacuum and a sufficiently narrow capillary, is so extremely sensitive that it must be used in a special room, because in every chemical laboratory considerable mercury vapor is present, enough to contaminate the gold sheet in a short time and at least render the green line of the mercury spectrum visible.⁶

More important than the Abel test is the heat test at 132°C., used by the German Railway Administration as the official stability test for nitrocellulose intended for the manufacture of smokeless powder suitable for transportation.

To make this test qualitatively 2 grams of dry nitrocellulose is heated in a glass tube 35 cm. long in a liquid bath to 132°C. and the time noted at which the first visible decomposition products, such as yellow vapors, are given off. This should not occur within one hour. Back of the test tube there is a sheet of white paper to make observation of the yellow vapors clearer.

In carrying out the test quantitatively (decomposition test⁶) the decomposition products split off within a definite time are measured as NO. The apparatus necessary for this and the method of carrying out the determination are described as follows in the "Regulations regarding the Testing of Explosives According to Section C. Ia of the Railway Traffic Regulations" of the former Railway Administration (fig. 29 a, b, c, d)

The apparatus for heating the tubes consists of a closed copper vessel (a) 35 cm. wide, 10 cm. deep and 25 cm. high, closed air tight by a cover (b) by screws and soldered, also tubes (c) 20 cm. long and 2 cm. internal diameter, drawn from heavy brass and ten in number, used to hold the glass tubes inserted, also a thin tube for the thermometer (d), and finally a copper condenser (e). The device is heated by a Koch safety burner. The temperature is maintained constant at 132°C. Constant temperature can best be maintained by boiling gently in the copper box a liquid which boils at 132°C., such as commercial amyl alcohol or a suitable xylene mixture.

⁶ See also Kast, *Spreng- u. Zündstoffe*, p. 142 (1921); Dupré and Andre, *Arms and Explosives*, p. 15, 32, 47, 61 (1907); *Z. Schiess- und Sprengstoffw.* (1910) p. 81.

⁶ According to Bergmann and Junk.

The glass tubes used to hold the nitrocellulose (*f*) must be thick-walled and sealed at the bottom, 35 cm. long, 2 cm. external diameter and an internal diameter of 1.5 to 1.6 cm. They must have a mark on them at 50 cc.

The dome consists of a glass beaker (*g*) 10 cm. high and 3 cm. internal diameter, with a glass tube (*h*) passing through it, which at the bottom swells out to a stopper ground into the heating tube. Above the tube in the inside of the glass beaker is a small glass tube (*i*), blown out to a bulb in the center of the beaker. The beaker (*g*) is half filled with water.

Instead of the beaker head a bulb head of the form shown can be used. This is filled with water up to the lower part of the upper bulbs (fig. 29b).

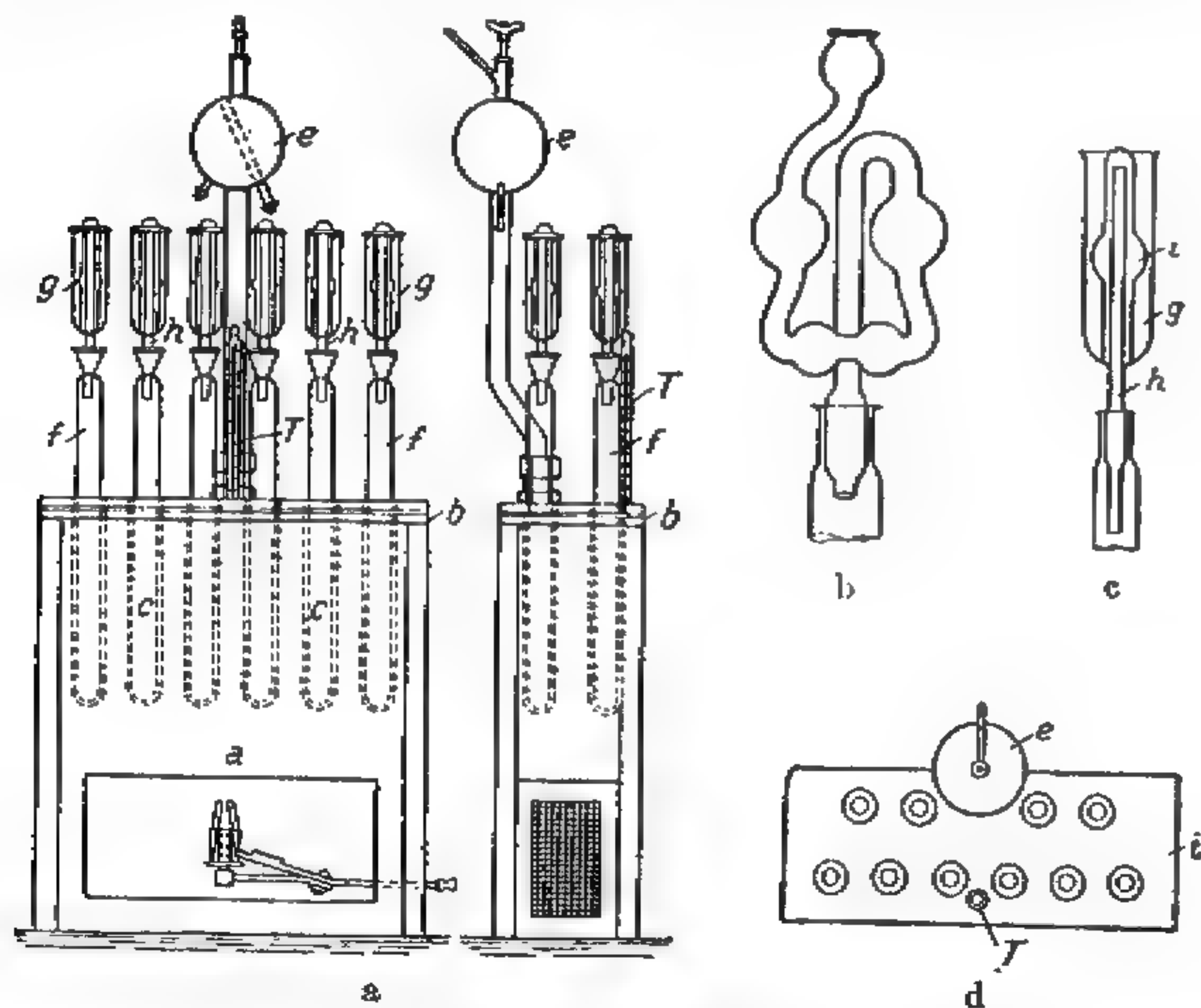


FIG. 29a. GERMAN RAILWAY HEAT TEST APPARATUS.

FIG. 29b. GLASS TRAP. FIG. 29c. GLASS TRAP. FIG. 29d. PLAN

In testing unstable nitrocellulose explosions are not impossible. The heating device is therefore built into a housing, in the front and back of which are double glass windows 8 to 9 mm. thick, separated by round rubber strips.

For the test only nitrocellulose well dried (at 40 to 50°C.), with a maximum of 1 per cent moisture, is used. The moisture content is determined by drying a special sample of 2 grams for two hours at 100°C.

Carrying out the test. Two grams of dried nitrocellulose is placed in the heating tube by means of a metal funnel. The portions adhering to the walls are removed by jarring or by a feather. The ground stopper of the head is carefully greased, fitted into the tube, the top device filled with water, and the

tube placed in the heating device previously brought to 132°C. After two hours the tube is removed from the device. On account of the cooling the water runs from the head piece into the tube and saturates the nitrocellulose. When using the bubble tube it is necessary to add some water after the heating is ended, in order to cause the water to run into the heating tube. The head piece is then washed out, and the tube filled up to the mark and shaken vigorously. The contents of the tube are filtered through a dry filter into a flask. The nitrogen content of 25 cc. of the filtrate is then determined after adding 1 cc. of normal potassium permanganate by the Schultze-Tiemann (Schlössing) method. In this to collect the gases a measuring tube is used whose upper part (10 cc.) has a smaller diameter so that tenths of a cubic centimeter can be read with accuracy. The volume of nitric oxide is reduced to 0° and 760 mm. and corrected for the pressure of water vapor. The 25 cc. of the filtrate correspond to 1 gram of the nitrocellulose used. The amount of nitric oxide evolved from this quantity should not be more than 3 cc.

The ignition point of collodion cotton, determined in the same way as with nitroglycerine, should be above 180°C. with 0.05 to 0.1 gram samples. The German railway regulations specify 0.1 gram and heating the oil bath from 100°C. by 5°C. per minute, so that 16 minutes after insertion of the samples 180°C. is reached.

Solubility in ether-alcohol. Although there seems to be no parallel between the solubility of a collodion cotton in ether-alcohol and in nitroglycerine,⁷ in general nitrocellulose very soluble in ether-alcohol also dissolves well in nitroglycerine and is suitable for its gelatinization.

While an absolutely clear solution of collodion cotton in ether-alcohol is required for photographic purposes, this is in no way necessary for the manufacture of explosives. A content of several hundredths insoluble nitrocellulose is no bar to its use for this purpose.

Solubility determination. Two and one-half grams of nitrocellulose is treated in a 250 cc. graduated cylinder having a glass stopper with 250 cc. ether-alcohol (1 volume absolute alcohol and 2 volumes absolute ether) for twelve hours with frequent shaking. To avoid lumps, which hinder and delay solution, the alcohol is first poured on the nitrocellulose, shaken well, and then the ether added gradually while shaking. After a suitable settling from the insoluble material, 50 cc. of the supernatant, clear solution is removed by a pipette to a weighed beaker and the solution allowed to stand and evaporate in a warm place.⁸ The addition of some water facilitates the formation of a

⁷ Silberrad, *Z. angew. Chem.* (1906), p. 2051.

⁸ Filtration and direct determination of the insoluble residue is impractical because the colloidal solution, even after decanting the main portion and dilution of the residue by additional ether, is very difficult to filter.

pulverent residue and consequently the drying. Finally it is dried to constant weight at 50°C. while covered by a watch glass, cooled and weighed quickly. The residue, multiplied by 5, represents the soluble nitrocellulose contained in 2.5 grams of collodion cotton.

Viscosity. Naturally the viscosity of ether-alcohol solutions of collodion cotton is primarily a function of the concentration. It can vary widely, however, even at equal concentrations, depending upon the method of manufacture. Since it is apparently dependent upon the molecular state or molecular size of the collodion cotton, it is more or less independent of the nature of the solvent and the viscosity of nitroglycerine-collodion cotton solutions runs parallel to solutions of collodion cotton in ether-alcohol. A high viscosity thus means that the required solidity of the nitroglycerine gelatine is obtained with a small amount of collodion cotton.

According to Lunge and Suter⁹ the viscosity has no direct relation to the nitrogen content, but reaches its maximum at the highest nitrogen content, decreases with rising temperatures of nitration and increasing times of nitration, and decreases with increasing water contents of the nitrating acids. The highest viscosities are obtained with nitrating acids low in water and at short nitrating periods. Collodion solutions fall appreciably in viscosity in a short time if they contain only slight traces of acid.

The viscosity can be determined in various ways, for example by measuring the time required for the solution to run out of a burette, or by measuring the time required for a hollow glass sphere or a bubble of air¹⁰ to rise through the solution from a certain mark.

In all such comparative measurements the temperatures must be kept constant, since the viscosity of a given solution varies greatly with the temperature.

Gelatinizing power. The ability of a collodion cotton to bind nitroglycerine to a homogeneous, solid mass when present in small quantities, is measured by the so-called gelatinizing test. Escales¹¹ describes this test as follows:

Two and one-half grams of collodion cotton, after drying, is put into 40 cc. of nitroglycerine, so that the latter contains 3.75 per cent of nitrocellulose. The mixture is well agitated in a copper cylinder and allowed to stand for ten

minutes, after which 1 cc. of a mixture of 3 parts methyl alcohol and 1 part acetone is added, the cylinder placed in warm water (70 to 75°C.) and stirred for about five minutes with a horn spatula. The originally thin liquid has then changed to a tough mass. After an additional twenty minutes the cylinder is removed from the water and allowed to cool. In about one-half an hour the gelatine must be of such a consistency that it can be lifted off the bottom by the spatula without losing its coherence and without leaving traces of nitroglycerine on the bottom.

To the knowledge of the author this test is made in German factories with even less nitrocotton and without the addition of a solvent. Two and one-half grams of finely screened collodion cotton is well stirred with 97.5 grams of cold nitroglycerine in a small porcelain casserole having a handle, the mass warmed by placing in a water bath at 65°C., and kneaded twenty minutes while warm with a horn spatula. After cooling, the mass should separate readily from the porcelain as coherent lumps when taken up on a spatula. In such a case the gelatinizing power is called I, and a lower degree which does not give a coherent, cohesive gelatine with this quantity is expressed by the corresponding grade marks II to V. Estimation of the suitability of a collodion cotton for the manufacture of blasting gelatine and gelatine dynamite by this rather crude method is wholly a matter of experience.¹²

In any case, collodion cotton which gives a very sticky or oily, non-cohesive gelatine in this test presents the possibility of exudation of nitroglycerine from dynamite on long storage, particularly on warm storage.

Improvement in gelatinizing power. The gelatinizing power of collodion cottons which do not give complete gelatinization in small quantities or even when used in larger amounts, or those which exude nitroglycerine during storage, such as were obtained during the war by nitration of wood pulp on account of the shortage of cotton, can be improved by certain additions, mainly the so-called Centralites, tetra-substituted urea derivatives, so named by the Zentralstelle für wissenschaftlich-technische Untersuchungen in Neubabelsberg bei Berlin, which was first used as a stabilizer of smokeless powder. This product, also used as a non-volatile camphor substitute and which itself can gelatinize nitrocellulose, has the peculiar property

⁹ *Z. angew. Chem.* (1906), p. 2051.

¹⁰ Coochius Viscosimeter, used by Lunge.

¹¹ *Nitroglycerin und Dynamit*, p. 228.

¹² In the United States some factories actually make blasting gelatine on a small scale in a model mixer to test the suitability of collodion cotton.—
TRANSLATOR.

of facilitating the gelatinization of nitroglycerine when present in small quantities (1 to 3 per cent of the nitroglycerine) and improving considerably the permanence of the gelatine, even when using poorly gelatinizing collodion cotton.¹³

Centralites 1, 2 and 3, i.e., di-ethyl-di-phenyl-, di-methyl-di-phenyl- and ethyl-methyl-di-phenylureas come into this consideration. These products were brought out by the firm Weiler-ter-Meer at Urdingen am Rhein under the name of Mollites.

British patents 14658 of 1915 and 126056 claim the same effect in gelatinizing nitroglycerine by collodion cotton, and propose as general addition agents the substituted ureas, for improving the gelatinizing power. According to these patents gelatinization is facilitated and takes place without heating.

Dinitroglycerine and nitroglycol have the peculiar property of giving firm gelatines in a comparatively short time at ordinary temperatures. When using nitroglycol in place of nitroglycerine this is of particular importance on account of the ready volatility of the nitroglycol.¹⁴

On the other hand, there are substances which adversely affect the gelatinizing power and counteract gelatine formation, and which are therefore to be avoided as components of gelatine dynamite. Anthracene oil is in this class. When present in only a few per cent, it destroys the gelatine, rendering it crumbly and causing exudation of the nitroglycerine.

Nitrogen content of collodion cotton. Since the collodion cotton is an active component of the explosives in question a high nitrogen content, or a high degree of nitration, is naturally desirable. The collodion cotton used for the manufacture of dynamite, the so-called dynamite cotton, as a rule has a nitrogen content of 12.1 to 12.2 per cent and is therefore a mixture mainly of ennea- and decanitro-cellulose.

Drying collodion cotton. After preparation collodion cotton is separated from the excess of water by centrifuging and is usually stored and transported in a moist condition containing about 35

¹³ German patent application C.29014/78c, April 22, 1920.

¹⁴ On the other hand, nitropolyglycerine gelatinizes less easily with the collodion cotton as ordinarily made, and since this type of nitroglycerine is used very largely in the United States the gelatinization tests are made with nitropolyglycerine instead of nitroglycerine.—TRANSLATOR.

per cent of water, in zinc-lined wooden boxes. It is usually dried completely before gelatinizing.

It is possible to carry out the gelatinization process with moist collodion cotton, and many factories do so, in order to save the cost of drying and avoid the danger of handling dry collodion cotton. However, the presence of moisture hinders the process, particularly the uniform, fine distribution of the nitrocellulose in the nitroglycerine and so the production of an absolutely homogeneous gelatine, so that moist collodion cotton must be carefully rubbed through a comparatively fine screen to prevent the formation of lumps in order to obtain absolute homogeneity, or a subsequent exudation of nitroglycerine is to be feared. While the water is displaced from the nitrocellulose by the oil (nitroglycerine) during gelatinization and largely evaporated, so that the remainder of it does not affect the explosive unfavorably, proportioning the moist collodion cotton requires some care, since it dries rapidly in the air. For these reasons it is preferable to dry the collodion cotton and to incur a certain amount of risk in handling the dry product, and meet such a danger as far as possible by the best possible drying devices.

Drying gun cotton and collodion cotton, and dry houses used for this purpose have been described at length by O. Guttman,¹⁵ and up to the present time hardly anything in this process and apparatus has been changed. The wooden dry houses are surrounded by barricades. The collodion cotton is spread out on trays in layers 4 to 5 cm. thick. Often the bottoms of the trays are of copper or bronze wire screen, connected to the ground in order to carry off the accumulated charge of static electricity. This is advisable when a constant current of air is passed over the nitrocellulose.

Wooden trays are also used, on which the material is simply spread out, strong air currents being avoided, the nitrocellulose being dried gradually in heated rooms, which requires several days. The temperature should not exceed 40°C., and warm water heating is preferable. The control thermometers should be visible from the outside.

The heaters are so arranged that the collodion cotton dust has as little access to them as possible. The same is true of the floor, which should preferably be covered with linoleum. The door and window sills should be washed off daily.

To avoid loss of heat the houses have double walls, with insulating material between them, such as cinder or ash.

The whole arrangement and handling is intended to avoid as far

¹⁵ *Industrie der Explosivstoffe*, pp. 363-368.

as possible any friction, since the dry collodion cotton is particularly sensitive to friction when warm. The workmen wear felt shoes when entering the room. It is also best to empty the trays only after they have cooled.

With uniform conditions and uniform charges the completion of drying is known from experience, but this can be controlled by removal of samples and determination of their moisture content in the laboratory by heating for one hour at 100°C. If this moisture content is not over 0.5 per cent the collodion cotton is sufficiently dry, and it is then taken to an adjacent room and put through a 3 to 4 mesh screen into boxes, not by rubbing but by a gentle shaking.

Dry collodion cotton is hygroscopic, and absorbs up to 2 per cent of moisture. This, however, is of no particular importance for dynamite manufacture, but it is often packed in water-tight zinc-lined containers or water-proof sacks. In many plants it is weighed out into pasteboard cartons, which are covered with a pasteboard cover and taken directly to the gelatinizing house and used.

PREGELATINIZING; GELATINIZING HOUSE

If the mixing is done in heated mixers and the real gelatinization done here also, the mixing can be preceded by a preliminary gelatinization at ordinary temperatures, or the real gelatinization can be done in heated gelatinizing pans.

In the first case the pregelatinization room contains storage tanks for the nitroglycerine, into which the latter runs directly from the wash house, and in the center or on both sides a row of rectangular, hard rubber lined wooden boxes on frames, holding about 25 kg., into which the nitroglycerine is poured from hard rubber buckets or hard rubber cans. The collodion cotton is then added and mixed by hand to a uniform paste, which is allowed to stand a longer or shorter time, as may be required. The last mix of the day may be allowed to stand over night. On standing a short time the paste remains a thick liquid, but on standing over night it turns into an incomplete gelatine, which only becomes a real solid and elastic material in the subsequent kneading while warm.

The boxes are carried into the mixing house on handbarrows and their contents emptied into the mixer.

Pregelatinization can also be done warm, as is customary in German plants. In this case there is a row of rectangular, double-

walled copper pans on low supports on each side of the gelatinizing house, through the hollow walls of which warm water at 60 to 65°C. passes, so that the contents reach a temperature of 45 to 50°C. during the course of gelatinization.

Such a gelatinizing pan 80 cm. total height, 100 cm. wide, 135 cm. long, 30 cm. deep, and with a rim about 10 cm. wide, holds a normal charge of 100 kg.

A thermometer is placed at the warm water inlet of the pan. The valves for regulating the flow are located at convenient points as far removed from the pan as possible, and are frequently cleaned of collodion cotton and powder dust by washing with a wet rag, as are the pipes and exterior of the pan. The warm water tank, which must be provided with automatic regulation of steam supply so that its contents will not rise above 70°C., is outside the building on top of the barricade. It is preferable to connect it to a warm water pipe and feed it with water at 65 to 70°C.

The nitroglycerine and collodion cotton are stirred in the pans by wooden shovels or by hand, and after completely uniform distribution the mixture is allowed to stand twenty to twenty-five minutes. The gelatine is then put into wooden troughs and taken to the mix house.¹⁶

MIXING GELATINE DYNAMITE

To obtain complete homogeneity the blasting gelatine so prepared is well mixed in a mixing machine, where it is blended with the mixed absorbents in the case of gelatine dynamite. Two types of mixers are used, one the George McRoberts, English type having the shape of a copper, bronze or brass trough in which two agitators revolve on vertical axes. This is much used in England as well as in Germany, in factories which make mainly blasting gelatine and gelatine dynamite for export. It is suitable only for very gelatinous explosives and those high in nitroglycerine. Other German factories use mostly the so-called Werner-Pfleiderer.

¹⁶ In the United States a collodion cotton is made and used which does not require such long mixing to gelatinize. The nitroglycerine is run into the heated mixer and the collodion cotton added. This is mixed by the mechanical stirrer for only a few minutes to obtain practically complete solution, the absorbents added, and the whole mixed to a gelatine dynamite. Collodion cotton suitable for use with nitroglycerine is not suitable for nitropolyglycerine mixtures, used almost universally in the United States.—TRANSLATOR.

The McRoberts machine is described by O. Guttman¹⁷ as follows:

"It consists of a strong frame (a) of oak, on which a false bottom (b) can be raised or lowered by the aid of two threaded rods (c). These latter fit into nuts in the side walls of the bottom and project upward as smooth shafts having bevel gears (e) fastened on the top. Above the apparatus a horizontal shaft (f) with two bevel gears (g) engages the vertical shafts. Turning

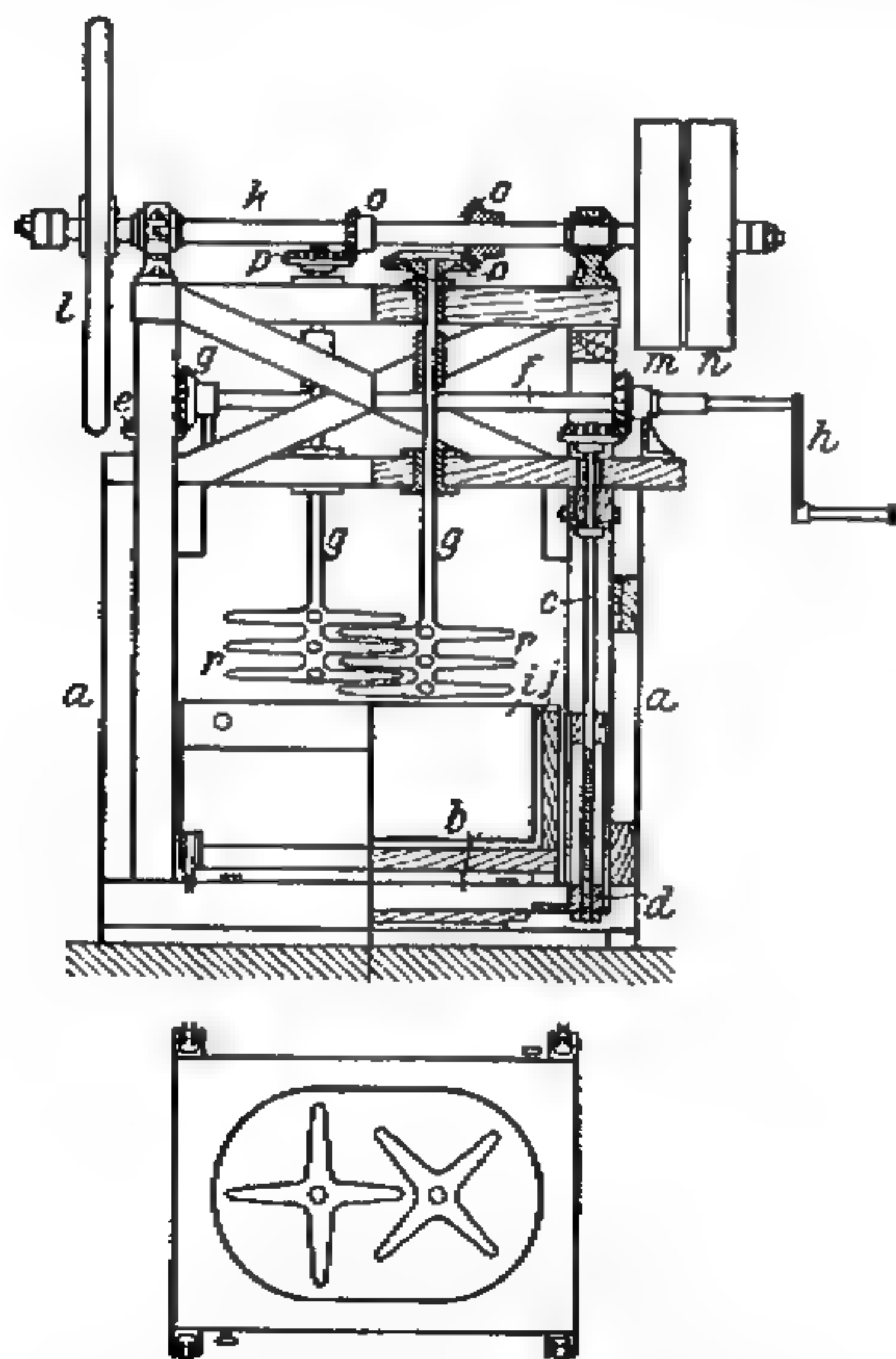
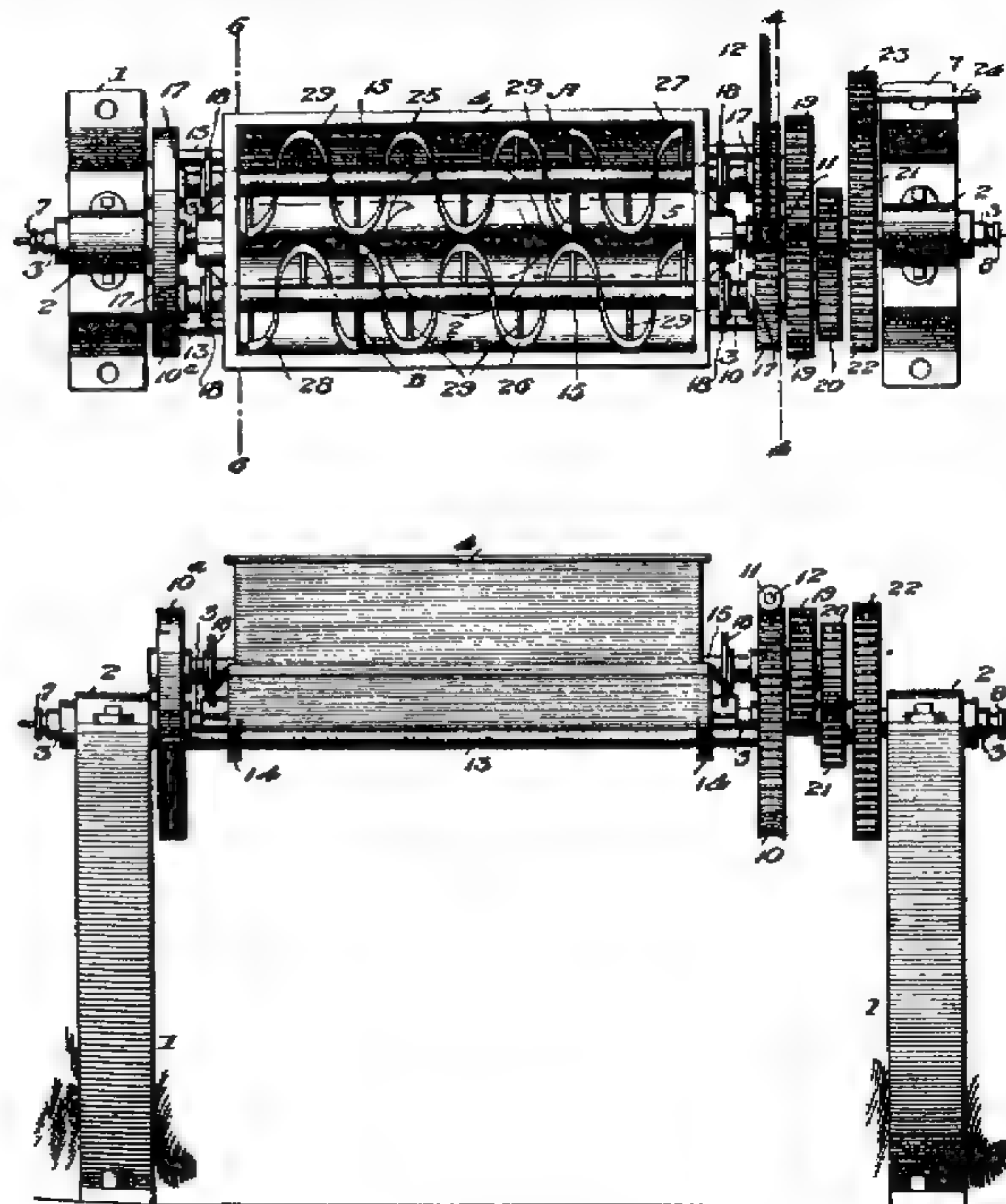


FIG. 30. McROBERTS GELATINE MIXER

the handle (h) raises the false bottom by the threaded shafts. On this false bottom is placed a copper pan (i), movable on four wheels and having a water jacket (j) which can be connected to a warm water pipe by a rubber hose. The frame is extended at the top and carries a second horizontal shaft (k) having a balance wheel (l) and a tight and loose pulley (m and n) and two bevel gears (o). The latter engage corresponding bevel gears (p) attached

¹⁷ *Industrie der Explosivstoffe*, p. 500.

to the vertical shafts (g) projecting through the frame. The latter have finger-shaped, cross-blade stirrers (r), so arranged that the blades of the two stirrers move in and out of one another somewhat like a Root Blower, as is



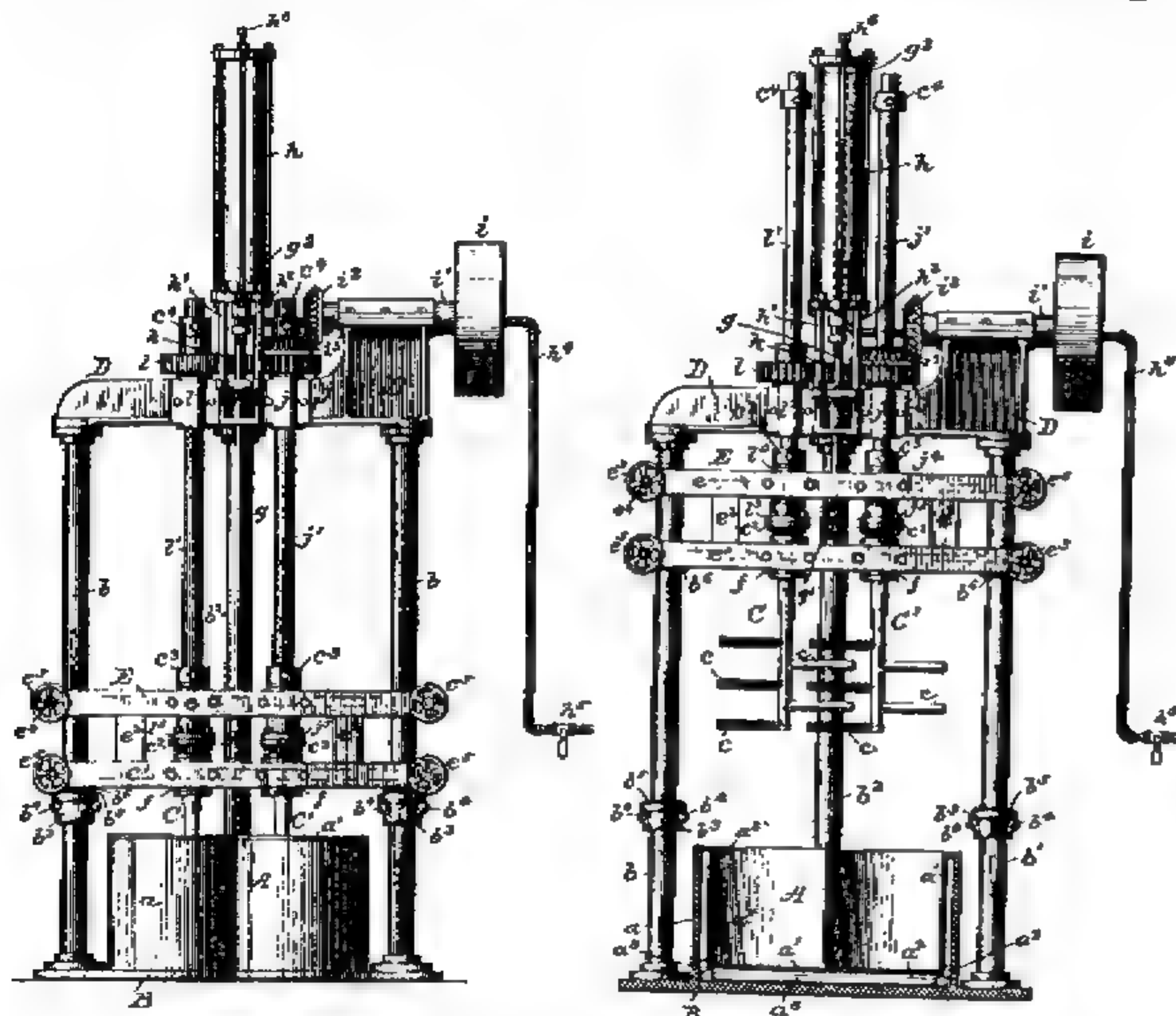
TALLEY MIXER

United States patent 946475

evident in figure 30. The operation of the machine is as follows: The carriage with the double-walled pan is pushed on to the false bottom, the pan connected to the warm water pipes and raised into position by turning the handle until the stirrers are immersed. The operation then continues by the stirrers.

The temperature of mixing is maintained between 40 and 45°C., and the operation is finished within an hour.¹⁸

The mixing house of a large German dynamite plant contains six such machines, made of brass, three on each side of the building.¹⁹



GELATINE MIXER
United States patent 677803

Raising and lowering the pans is done automatically and very slowly by electrical drive. The charge in the pans is 100 kg. (220 pounds).

¹⁸ Somewhat similar machines are used in the United States. They do not have the means of sliding the heated bowl in and out of position, the latter being fixed in place. They mix 500 to 550 pounds (227 to 250 kg.) at a time, and the whole operation *including preliminary gelatinization*, requires less than an hour, see United States patent 677803. They are now being gradually replaced by the so-called Talley machines, which mix about 1500 pounds (682 kg.) in about the same time or even less and discharge mechanically, see United States patent 946475.

¹⁹ United States practice has mainly limited the number of gelatine mixers in a building to two, and the preferred practice is one, in order to limit the risk.

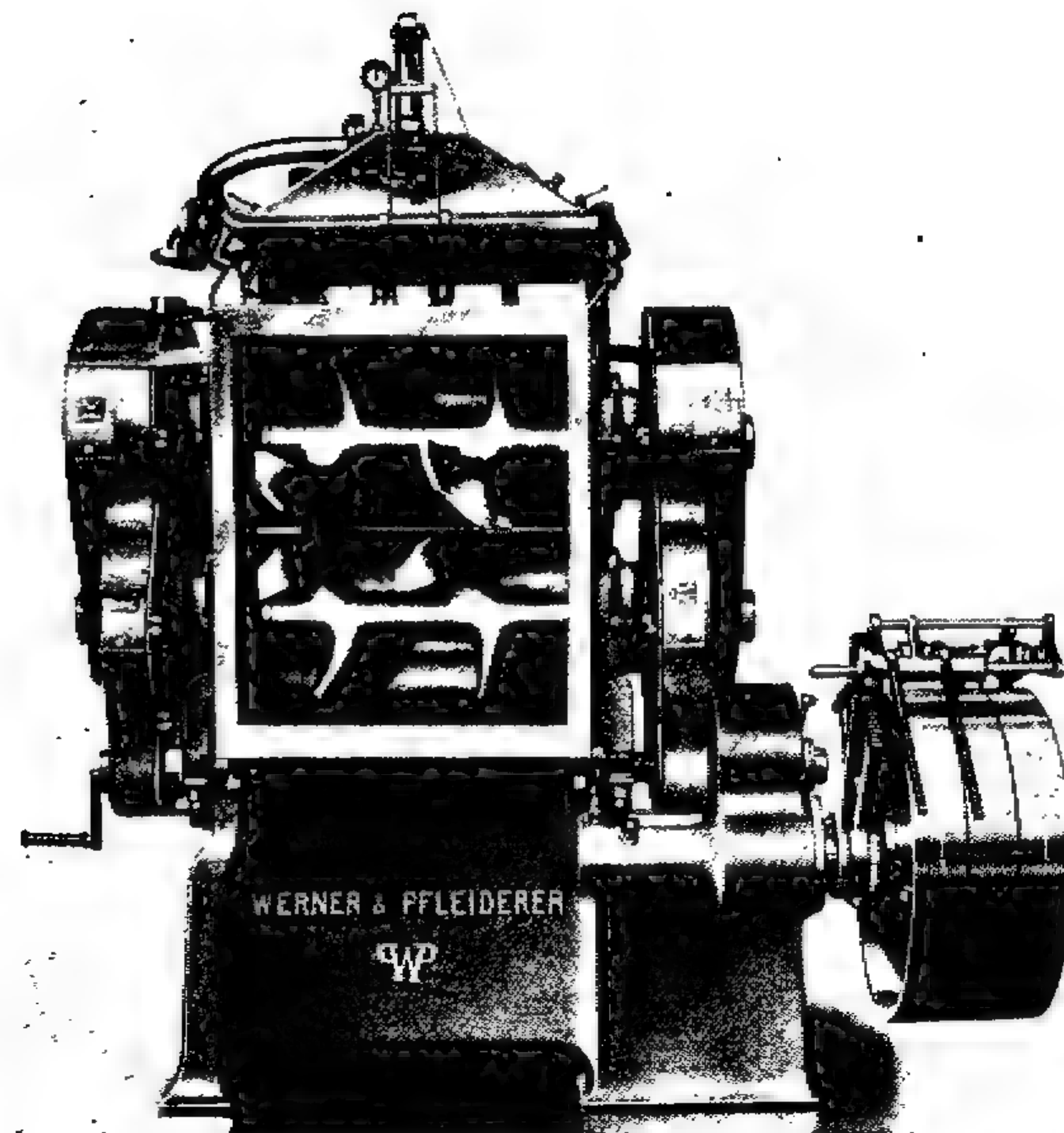


FIG. 31. WERNER AND PFLEIDERER GELATINE MIXER

Many consider this device safer than the Werner-Pfleiderer machine, since the space between the fingers of the stirrers and the walls is greater than between the stirrers and walls of the latter, so that a dangerous pinching of any hard, foreign substance such as nails, screw heads, etc., which might accidentally get into the explosive, is less probable. However, Guttman (*loc. cit.*) does not exclude the possibility of heavy shocks and dangerous breakages in the English construction. One disadvantage is the long time of mixing, amounting to about one hour for absolutely uniform mixing of the absorbent, while the paddles of a Werner-Pfleiderer machine mix far more efficiently, so that a homogeneous mixing is obtained in ten to twenty minutes, depending upon the velocity of rotation, assuming, however, that a pregelatinization has been made in a heated pan.

The Werner-Pfleiderer mixing machine resembles those used for bread-dough mixing. The bronze mixing trough is semicircular at the bottom, and two horizontal shafts carry two mixing blades side by side. Usually the trough consists of two adjacent bowls or semicylinders with a ridge between them, so that each semicylinder has a shaft through it. The internal construction of such a mixer is shown in figure 31. Usually the mixer is covered with a lead jacket on the outside, through which warm or cold water can be circulated to heat or cool it.

The mixing blades are revolved at various speeds by corresponding gears, and can be driven either simultaneously or separately. Usually one shaft turns twice as fast as the other.

In order to reduce the friction of the mixture on the shaft openings the shafts are arranged with a certain amount of play or space so that the mixtures which contain liquids, or thin gelatines, can always run through, be collected from time to time, and returned to the mixing.

The drive is electrical by pulleys and transmission, the switches being outside the building, so that during the operation of the mixer no operator need be in the building, a precaution which is not universal.

There should be a space of at least 3 mm. between the mixing blades and the bottom, so that any hard, foreign substance accidentally in the mass may not be pinched and develop a dangerous friction. This can be avoided for the most part by passing all the components of the mix through a screen just before mixing, either having a screen

directly over the gelatinizing pan or mixer or bringing the components from a screening room to the mix house in well covered, closed vessels.

With large clearances between the walls and mixing blades it is conceivable that parts of the plastic mass stick to the walls and escape thorough mixing.

In order to still further reduce the danger of sudden, violent friction and possibly avoid it altogether, use has recently been made of the so-called overload relay, which on increased resistance within the mass, or increased current consumption, cuts off the electric power immediately and stops the machine. It consists of a watt meter, whose pointer makes a contact at a certain degree of increased resistance, closing a circuit which in turn activates and electromagnetic cutout.

In order to be able to empty the trough conveniently the latter is tipped, i.e., revolved about one drive shaft, by hand with small machines, by power with large machines. Since the drive shafts remain in position the mixing blades continue to revolve, no matter whether the trough is horizontal or vertical, so that the trough is emptied by the action of the machine itself into wooden boxes placed below it. An exact description of the construction of the mixer and the emptying device is given by Guttman.²⁰

Machines²¹ are built with a capacity of 50, 100 and 200 kg. (110, 220 and 440 pounds). They are made for experimental laboratories in 1 and 3 kg. sizes to prepare small quantities of explosives on a works scale. A mix house usually contains one or two machines.

The Draiswerke "Säulenketmaschine," recently come into use, in which pregelatinization and mixing are done in one and the same machine, will be described in the section on gelatine dynamites.

CARTRIDGING GELATINIZED EXPLOSIVES

The finished blasting gelatine or gelatine dynamite is taken to the cartridgeing house in long, shallow wooden boxes, broader at the top

²⁰ *Industrie der Explosivstoffe*, pp. 520-524.

²¹ In the United States a so-called Talley Mixer is widely used. It resembles a Werner-Pfleiderer machine except in having mixing blades shaped like long, spiral copper ribbons, revolving in opposite directions. It is emptied like the W & P machine. Its capacity is about 1500 pounds (682 kg.). - TRANSLATOR.

than at the bottom, and holding up to 50 kg. (110 pounds). Gelatinous explosives cannot be packed into cartridges in tamping machines, like the pulverent dynamites, but is done usually by screw presses.

The cartridgeing machine most widely used in the large English plants has been described by McRoberts and is shown in figure 32. It consists of a funnel-shaped housing (a) with a filling funnel (b), to which is screwed a nozzle (c) corresponding to the diameter of the cartridge to be filled, sometimes having a brass shell corresponding to the length of the cartridge. In the housing a shaft (e) and a screw (f) moves, carried by two bearings (dd) outside the housing, which forces the gelatine coming from the filling funnel, into which it is pressed from time to time by a wooden plunger, into the nozzle, gradually forcing it out of the latter in the shape of a sausage. Inside

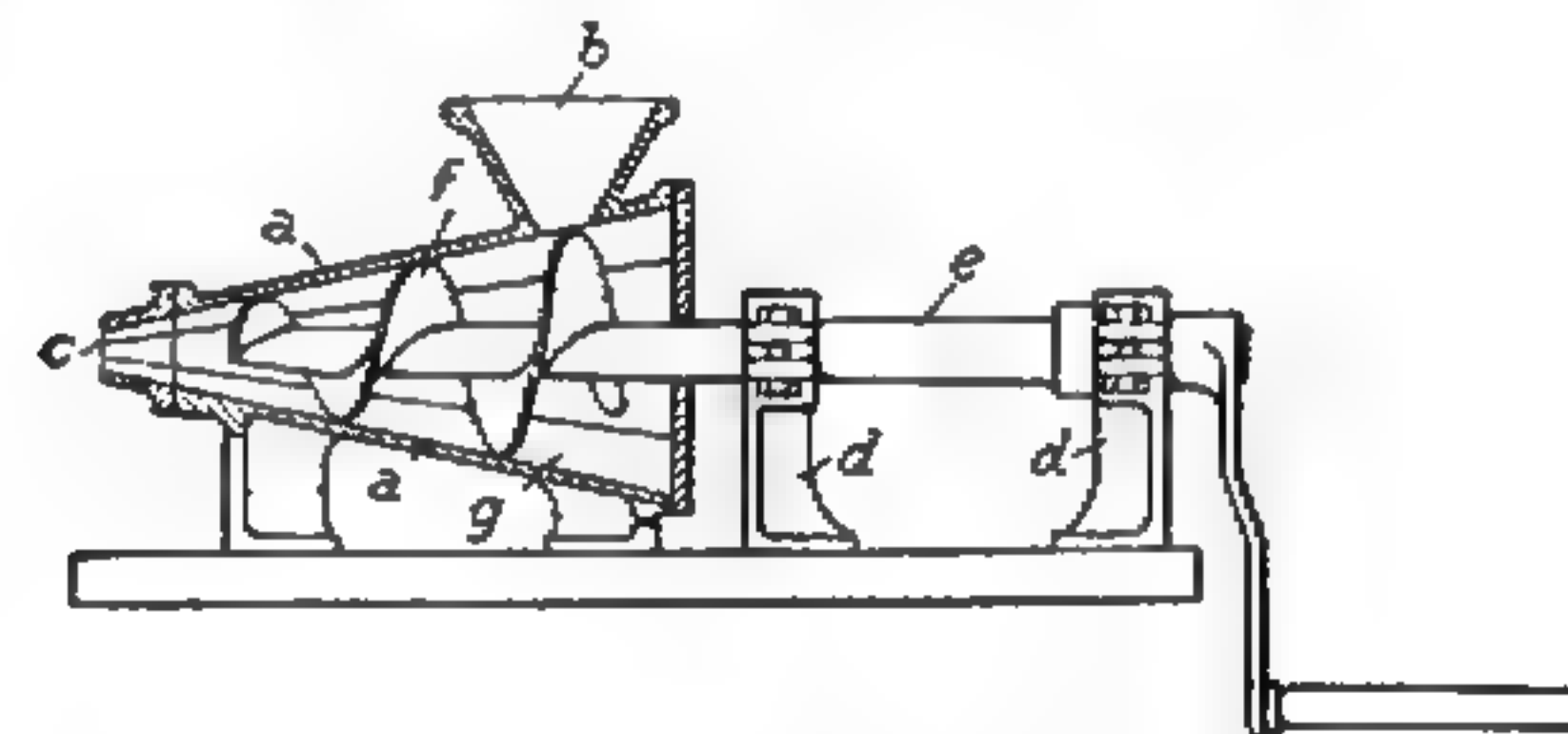


FIG. 32. SAUSAGE MACHINE FOR PACKING GELATINE

the housing there are ridges (g) to prevent the mass from revolving with the screw. The apparatus is mounted on a bed plate and the latter on a table. The machine is operated by two men, one turning the handle and from time to time pressing the gelatine into the filling funnel by a wooden plunger, the other man wrapping cartridge paper around the brass nozzle, folding it, and allowing the string of gelatine to flow out into the paper shell until the cartridge has attained the proper length. He then breaks off the string of gelatine and seals the cartridge at the open end. Often long strings of gelatine are forced out on a table, cut to proper lengths by a bronze knife, and then wrapped in paper. Parchment or paraffined paper is used for this purpose.

In Germany similar machines, but having a cylindrical housing, are used (fig. 33). The housings are usually somewhat conical at the

mouth, which raises the pressure somewhat and facilitates extrusion of the mass. On the other hand, the pressure in them is somewhat less than in those shaped like a funnel, which increases their safety. The nozzle usually has two, sometimes more, openings, so that several sausages or strings extrude from the press, which is particularly desirable with small diameters of cartridges.

Often the so-called "one strand" cartridging machine is used, operated by one man. In these there is a crank at the side on which the string of gelatine issues from the nozzle of the housing, so that the man doing the packing first extrudes the string of gelatine by turning the crank, then breaks the string of gelatine off and wraps the paper around it. The drive is via an extension shaft of suitable length and two gears.

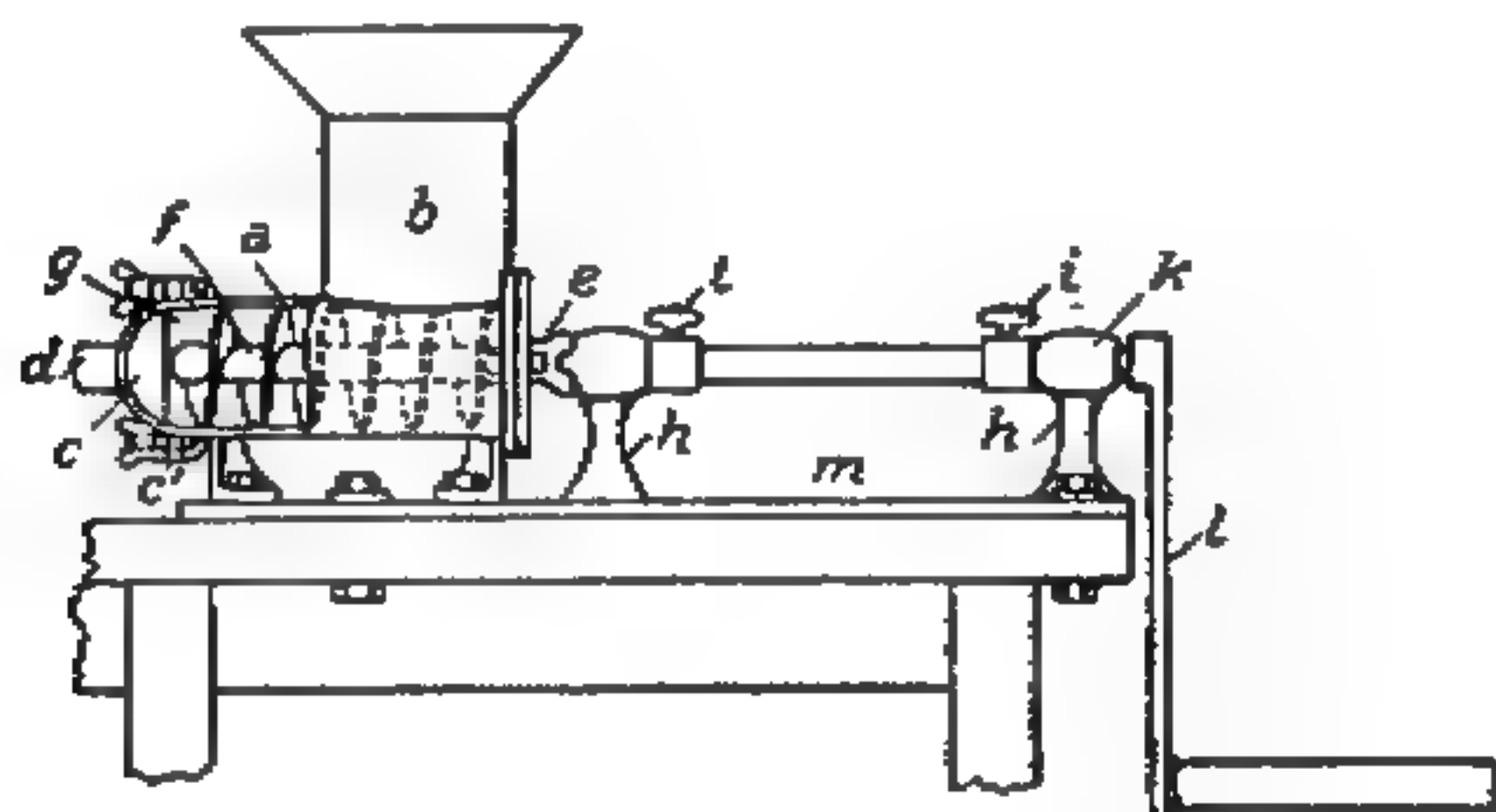
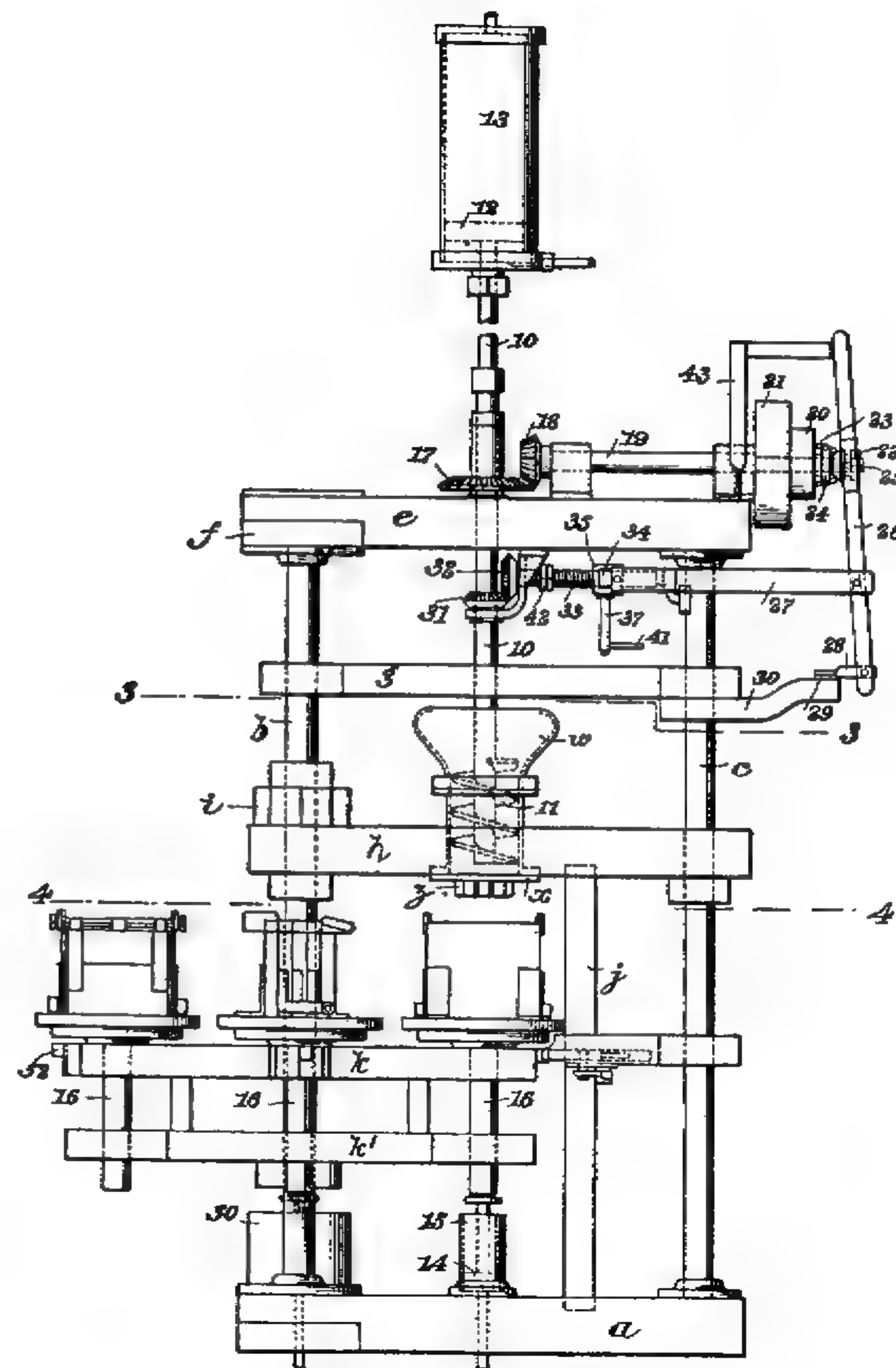


FIG. 33. IMPROVED SAUSAGE MACHINE

In the United States it is the custom to drive gelatine dynamite cartridging machines in plants by electric power.²² The extruded string of gelatine is carried on a traveling belt into an adjacent room, where it is automatically cut into pieces of suitable length and wrapped in cartridge paper.²³ For United States machines see illustrations below.

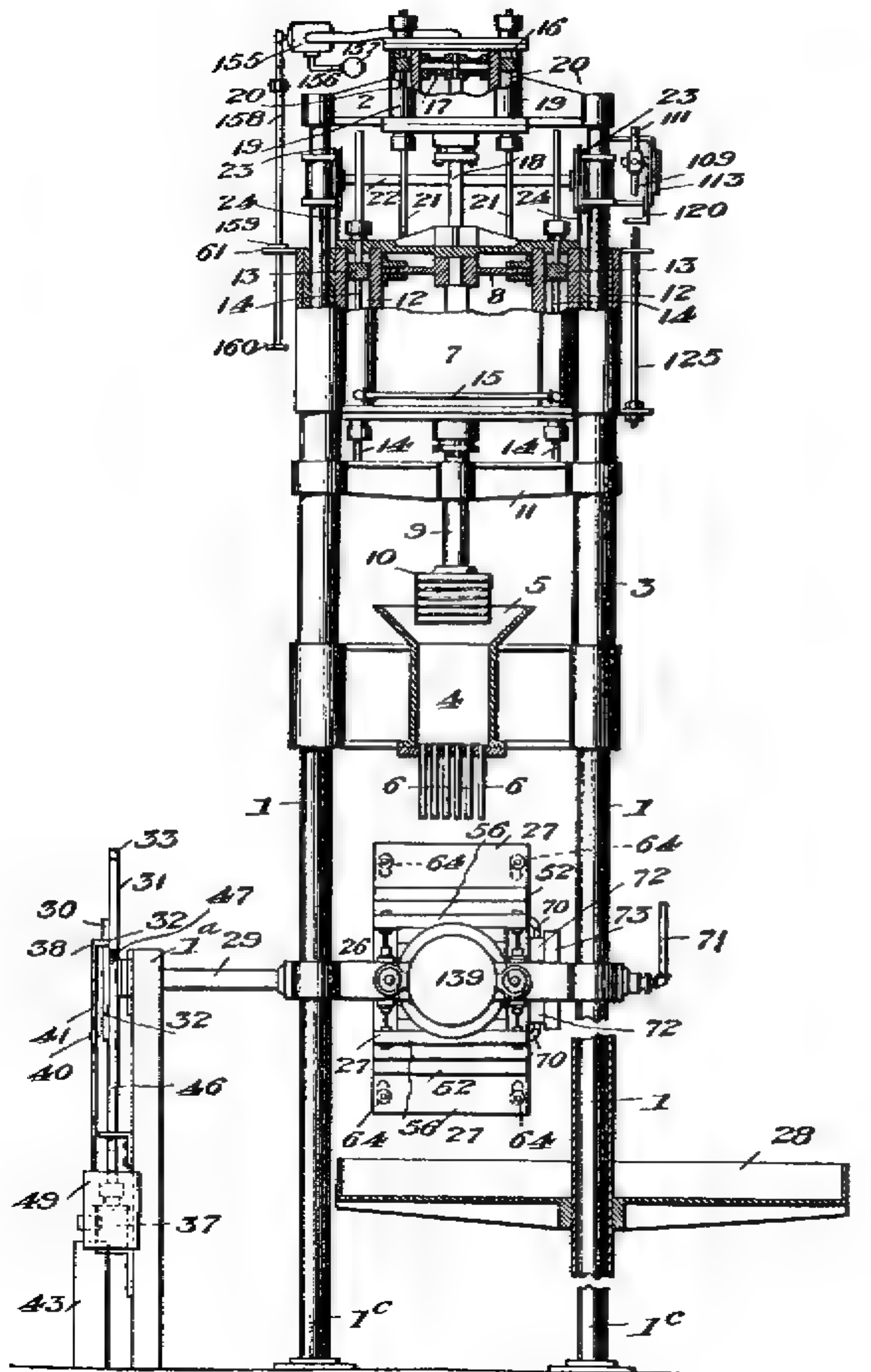
²² And now in England also.—TRANSLATOR.

²³ This is not the case. In the United States machines are driven electrically, but they are almost entirely automatic, the gelatine dynamite traveling up a conveyor belt to the hopper, where it is forced by a worm through a multiple nipple plate into already formed paraffined paper shells, the machine stopping automatically until a fresh lot of empty shells has swung into position, the open end of the filled shells closed automatically, and the finished cartridges discharged on to a table. With such a machine two men cartridge 12,000 to 15,000 pounds (5455 to 6818 kg.) per day of eight hours, depending



GELATINE CARTRIDGING MACHINE

United States patent 929815



GELATINE CARTRIDGING MACHINE

United States patent 1245528

In the case of blasting gelatine and gelatine dynamites, which today are only used in hard ore or rock, at least in Germany, where drilling tends to increase considerably in cost with the borehole diameter, very small cartridge diameters are usual. They begin with 18 and 20 mm. (0.71 and 0.79 inches). A diameter of 23 mm. (0.9 inches) is frequently used, and 25 mm. (1 inch) is not uncommon.

These screw cartridging machines can cause explosions if the gelatine accidentally contains hard, foreign bodies which can cause friction. In order to avoid this chance Norbert Ceipek proposed a centrifugal machine (German patent 117111) in which no sharp friction or sudden rise in pressure is possible. It consists of a centrifuge whose basket has tubes or nozzles on its periphery, to which the empty cartridges are attached or in which the latter are placed so that they can move. In the first case the density of the filling is determined by the number of revolutions chosen of the centrifuge, and in the other case by the number of revolutions and a resistance effect of the shell to displacement during the filling.²⁴ Thus a very rapidly revolving centrifuge would be required

TABLE 25

Compositions of blasting gelatine according to Kast

	GERMANY	AUSTRIA	ENGLAND	ITALY
Nitroglycerine.....	91.5	93	93-95	92-93
Collodion cotton.....	8.0	7	7-5	8-7
Soda or chalk.....	0.5	—	—	—

to force tough gelatine, for example, through the nozzles. Whether or not the use of a rapidly revolving centrifuge in connection with high explosives would actually increase the safety of the operation and not introduce additional risks of improper operation or breakage remains uncertain. These machines are not in use in Germany.

Composition of blasting gelatine. In table 25 Kast²⁵ gives the compositions used in the various countries, whereas Guttman²⁶ speaks of a composition containing 90 to 91 per cent nitroglycerine and 10 to 9 per cent collodion cotton in England, which on account of

upon size of cartridges. With a machine having a piston instead of a worm about 40,000 pounds, (18,200 kg.) has been packed with three operators.—TRANSLATOR.

²⁴ For a more detailed description and illustration see Escales, *Nitroglycerin und Dynamit*, p. 235.

²⁵ *Spreng- und Zündstoffe*, p. 296.

²⁶ *Industrie der Explosivstoffe*, p. 499.

the strict English requirements as to exudation, particularly for export to the colonies, is assumed to be the most usual. Material exported from Germany usually contains 8 per cent collodion cotton of high gelatinizing power.

In France the composition is 92:8 under the designation of Gomme supérieure or Gomme extraforte. In Belgium the same composition, called "dynamite-gomme A" is customary. A 94:6 mixture is not permitted in France on account of exudation.

Blasting gelatine containing camphor. Although blasting gelatine is comparatively less sensitive to shock on account of its elastic nature than guhr dynamite formerly used, it was soon attempted to make it still more resistant to mechanical influences, in order to obtain munitions of war as insensitive to projectiles as possible. This was accomplished by dissolving camphor in nitroglycerine, which reduced the sensitiveness to detonation of the latter and the gelatine made from it.²⁷ The quantity of camphor added was dependent upon the degree of reduced sensitiveness desired. Hess²⁸ reports at length on this. In Austria in 1878-1892 a so-called military blasting gelatine, consisting of 96 parts blasting gelatine 90/10 and 4 parts of camphor was made, which was subsequently displaced by Ecrasit as a military explosive.

In Italy 5 parts of camphor were added to 100 parts of a 92/8 blasting gelatine. A composition such as nitroglycerine 90 per cent, camphor 3 per cent, and collodion cotton 7 per cent was even used in the World War in Russia as a filling for trench mortar bombs. In Italy it was prescribed in 1914 as munitions for the pioneer troops.²⁹

Camphorated, desensitized blasting gelatine requires a stronger initial impulse to ensure detonation than ordinary gelatine requires. Special priming cartridges, such as a pulverent mixture of 60 parts nitroglycerine and 40 parts nitrohydrocellulose, or pure, compressed gun cotton, are used.

The desensitizing effect of a few per cent of camphor should not be overestimated, however, and it should not be forgotten that the ease of detonation is dependent to a great extent on the collodion content of the gelatine as well as on the combining power of the collodion cotton.

²⁷ German patent 5528, July 2, 1878 to Dyn. A.-G., vorm. Alfred Nobel & Co.

²⁸ *Mitt. Art.-u. Geniewesen* (1878), p. 217.

²⁹ *Z. Schiess- u. Sprengstoffw.* (1914), p. 414.

The statement of Escales³⁰ that a military blasting gelatine with 4 per cent camphor could not be exploded by a No. 8 blasting cap containing 2 grams of mercury fulminate or by a priming cartridge of compressed gun cotton, is not correct. It depends very much upon the collodion cotton content and the age of the gelatine. (Refer to sections on Ease of Detonation, Explosive Strength and Sensitiveness to the Falling Weight Test.)

PROPERTIES OF BLASTING GELATINE

Blasting gelatine is a solid colloidal solution of nitroglycerine and nitrocellulose. It is a yellow, translucent, soft, elastic mass, which can be cut, bent and pressed without permanently changing form. Its specific gravity is about 1.63. Even strong pressure causes no nitroglycerine to exude from it, and it is absolutely insensitive to water. On long contact with water the surface becomes milky, but the ease of explosion and the explosive strength do not change on long storage under water, because of the difficult solubility of the components. It is therefore used to advantage for blasting under water, as in rock blasting in rivers or harbors.

Toward shock, blows and friction blasting gelatine is less sensitive than liquid nitroglycerine or even guhr dynamite. The elastic mass to a certain extent absorbs the shock and forms a cushion between hammer and anvil. This becomes noticeable in large masses and moderate shocks where often no detonation occurs on the first blow. If the material is spread out in a thin layer by the first blow the second can easily cause an explosion.

According to Will the 2 kg. falling weight gives explosion with guhr dynamite at 7 cm., and with blasting gelatine at 12 cm.

Blasting gelatine freezes far more difficultly than guhr dynamite. However, if the crystallizing process is once started it freezes to a hard, white mass which loses all flexibility and elasticity. Then, in contrast to guhr dynamite, it is somewhat more sensitive to blows than when in a soft condition, as is shown mainly by the shooting (projectile) test.³¹

The sensitiveness to shock is dependent to a great extent upon the toughness of the mass and consequently upon the collodion cotton

³⁰ *Z. Schiess- u. Sprengstoffw.* (1914), p. 414.

³¹ Escales, *Nitroglycerin und Dynamit*, pp. 238-239.

content. A higher content of the latter acts in the same way as an addition of a desensitizing agent such as camphor to nitroglycerine.

The author determined the comparative figures, shown in table 26, with the 2 kg. falling weight on blasting gelatines containing 7 and 9 per cent collodion cotton and a camphorated blasting gelatine of the above-mentioned Italian composition (5 parts camphor per 100 parts blasting gelatine, or 92:8). The composition of this gelatine was 87.6 per cent nitroglycerine, 4.8 per cent camphor, 7.6 per cent collodion cotton. The falling weight was in each case dropped six times upon a fresh 0.1 gram sample between a small steel stamp and an anvil. (See table 20.) The difference between the 7 per cent

TABLE 26
Determinations by the falling weight test

HEIGHT OF DROP	BLASTING GELATINE 93:7	BLASTING GELATINE 91:9	CAMPHORATED GELATINE 4.8 PER CENT CAMPHOR
cm.			
12	----- /-	-----	-----
15	----- + -	-----	-----
20	/ - + + - -	--- / - -	- / - - - -
25		----- + -	----- / -
30		----- +	+ - - - + -

- Means no reaction; / means slight reaction and practically no report; + means complete detonation.

and 9 per cent collodion cotton gelatines is thus greater than that between the latter and the camphorated gelatine.

Chemical stability. The chemical stability of blasting gelatine in general corresponds to that of its nitroglycerine. At ordinary temperatures and at gentle heats it is unqualifiedly stable.

The German railway regulations require for dynamites and similar explosives, including blasting gelatine, that whole, unbroken cartridges be stored at 75°C. for forty-eight hours without red vapors being emitted. On continued heating at this temperature bubbles finally appear, with decomposition and evolution of nitric oxides. Only materials made from pure raw materials withstand this severe test.

Abel test. In the Abel test, upon which great weight is placed in England particularly, according to which the companies exporting

blasting gelatine and gelatine dynamite to England and to English colonies must test their products, the effect of the surface must be taken into consideration. If the prescribed quantity of the gelatinous, cohesive mass is cut into a few large pieces and placed in the test tube the reaction occurs considerably later than if the material were reduced to a fine powder with a neutral medium and its surface thus artificially increased.

The English method of making the test of blasting gelatine and gelatine dynamite is as follows: 3.25 grams of gelatine is thoroughly rubbed with 6.5 grams of talc in a wooden mortar with a wooden pestle. The talc has been previously washed in distilled water, dried in air free from acid and stored in a closed glass flask. The gelatine-talc mixture is placed in small portions at a time in the test tube, tapping the latter lightly on the table occasionally, until the filling amounts to 1½ inches in height. The test is then carried out in the usual way at 72°C. The reaction should not appear within ten minutes.

Blasting gelatine made from well stabilized collodion cotton and well purified nitroglycerine usually withstands this test not longer than ten to fifteen minutes, although the collodion cotton and the nitroglycerine before combining to a gelatine each gave slight tests only after thirty to forty minutes. Since the chemical stability cannot be affected by the purely physical reaction of solution, this test shows clearly how much the result of the Abel heat test depends upon the physical state of the substance and the method of making the test, which apparently limits the value of this test in some respects.

The moisture content of the sample tested is also important. If high, so that on heating there is considerable condensation on the walls of the tube above the water bath, the appearance of the reaction is retarded, since apparently the precipitated moisture takes with it the first traces of evolved nitrogen oxides. Thus, well-dried explosive gives shorter tests. For comparative tests or for uniform procedure all explosive samples should therefore be corrected by drying in a desiccator.

Physical stability; exudation. On great temperature changes, particularly if the collodion cotton content is too low or if the collodion cotton used is of insufficient gelatinizing power, blasting gelatine at times exudes small quantities of nitroglycerine. Liquid nitroglycerine increases the danger, and cartridges showing a tendency to exude should be used at once and with particular care.

In England, and particularly in the English colonies, where the question of exudation due to the hot climate is more important than in temperate zones, exudation is watched very closely by the authorities (Inspector of Explosives).

*Liquefaction test.*³² This test is decisive mainly in England. A cylinder whose length is about the same as the diameter, and whose ends are cut sharply, is cut from the blasting gelatine cartridge to be tested. The cylinder, without wrapper, is placed with its base on a smooth surface, such as a sheet of pasteboard, and held fast by a vertical pin through its center. The sample is stored continuously for six days at 29 to 32°C. During this time the height of the cylinder of gelatine must not diminish more than a fourth, and the upper, cut surface must retain its shape and sharpness of edges.

A general characteristic of absence of tendency to exude is designated by Guttman as the fulfilment of the following requirements: From the mass of blasting gelatine or gelatine dynamite no substance should separate which is of a lower consistency than the remaining material, no matter what the conditions of transportation, storage or use, or if the material is subjected three times to consecutive, alternate freezing and thawing, or to the above described liquefaction test.

In Germany the railway authorities require that blasting gelatine and gelatinous nitroglycerine explosives undergo no external change when whole cartridges are subjected to storage at 30°C. for five days, and they must exude no nitroglycerine.

A tendency toward exudation can generally be met by increasing the collodion cotton content or by using agents such as centralite, which increase the combining power of the collodion cotton available. However, there are here two opposing considerations, since by raising the collodion cotton content and toughness of the gelatine the ease of detonation and propagation of the blasting gelatine are affected adversely.

Behavior on heating; ignition; explosion point. Blasting gelatine, in contrast to liquid nitroglycerine, can be ignited very easily by a flame or spark from a fuse and burns very rapidly and violently with a hissing sound. The combustion of rather large quantities can easily cause explosion. When frozen even small quantities can

explode on burning. On heating above a certain temperature explosion occurs without fail. In the determination of the explosion point the rapidity of heating plays an important part. If a small sample (0.1 to 0.2 gram) is heated in the usual way in a beaker placed in a metal bath, the temperature starting at 100°C. and rising 5° per minute, the blasting gelatine explodes with a report like a pistol at 202°C., after emitting yellow vapors above 170°C. and copious brown vapors above 180°C. A 0.2-gram sample shatters the beaker. On more rapid heating still higher explosion temperatures are found, according to Guttman 240°C., but it should be noted that such figures have no practical value since the temperature of the sample cannot follow that of the thermometer quickly enough.

If small samples (0.1 gram) are heated very slowly, at 5° per minute, they usually decompose below the explosion point, emitting red vapors, the remainder puffing slightly at about 195°C. Naturally, on slow heating of large samples explosion can occur at even lower temperatures.

Explosion point of camphorated blasting gelatine. An error which was adopted by Escales from Guttman and by the latter from Hess, is that the so-called military blasting gelatine containing camphor does not explode on slow heating, but only burns and throws out sparks.³³ The author at least found that blasting gelatine containing 5 per cent camphor, heated in the usual way to 200 to 203°C., explodes at the same temperature as pure blasting gelatine, and just as violently.

Detonation by initial impulse; propagation of explosion. Blasting gelatine is rather difficult to detonate, as compared to nitroglycerine explosives which contain nitroglycerine absorbed in a liquid state, and it propagates detonation at a distance only slightly. While the wave of detonation propagates with more difficulty through liquids, particularly viscous liquids, than through pulverent explosives or explosive mixtures, and the former are more difficult to set off by an initial impulse, this is true to an even greater extent with colloids like blasting gelatine. Here the degree of ease of initiation is in direct proportion to the degree of toughness and stiffness of the gelatine, and thus in general to the collodion content. The higher the latter the more difficult the gelatine to detonate, and finally, at

³² Guttman, *Industrie der Explosivstoffe*, p. 655.

³³ Guttman, *Industrie der Explosivstoffe*, p. 504; Escales, *Nitroglycerin und Dynamit*, p. 246.

very high nitrocellulose contents, the brisant explosive is changed into the non-brisant propellant, smokeless powder, a relatively hard, horny, little elastic mass, very slightly elastic as compared to blasting gelatine, which, although consisting of the two brisant components nitroglycerine and nitrocellulose, can no longer be detonated by a blasting cap when in a finished state, at least in coarse aggregates. This property is only again acquired by grinding a coarse powder to a fine one. It is then the air enclosed between the particles of powder which carries the wave of detonation. Examples of such propellants are cordite, containing 60 per cent nitroglycerine and 40 per cent nitrocellulose, and ballistite, containing 40 per cent nitroglycerine and 60 per cent nitrocellulose. Each per cent of collodion cotton appreciably affects the ease of detonation, propagation of explosion and velocity of detonation. In the proportion of 93 parts nitroglycerine to 7 parts collodion cotton blasting gelatine is still very readily detonated, and at least when in a fresh state explodes with the weakest blasting cap, a No. 1, and propagates detonation even in 25 mm. cartridges to a distance of about 10 mm. With 9 per cent collodion cotton a No. 4 blasting cap is required, and propagation to an adjacent cartridge only occurs with a No. 6 blasting cap.

A quite general fact, observed with blasting gelatine in a quite characteristic manner, but which is found with all gelatinous explosives to a more or less degree, is that the sensitiveness to detonation diminishes with time, apparently as a result of a physical change of state. With blasting gelatine and gelatine dynamites after long storage, particularly in hot climates, a diminution of explosive strength and even failures have been observed. This is spoken of as "inertness." [Usually called insensitiveness in the United States.—TRANSLATOR.] The author has seen blasting gelatines which had been returned from Africa after being stored there for two years, which would not detonate completely when unconfined and which would not propagate to adjacent cartridges. Also the lead block expansion and the lead block crushing of this sample were unusually low, in spite of the unchanged chemical composition.

This behavior forms a problem for exporting factories particularly, since on account of the danger of exudation in hot countries they are instructed to not use too small quantities of collodion cotton in blasting gelatine and gelatine dynamites. Insensitiveness becomes greater the higher the content of collodion cotton and the tougher the gelatine when in a fresh condition, as is evident from the above.

For domestic gelatine dynamite, where the question does not have so great an importance as in the English colonies, partly on account of climatic conditions and partly because of less strict criticism, insensitiveness plays no noticeable rôle. The gelatines can be made comparatively "thin" at first, since the absorbents also take a part in absorbing and retaining the oil.

An explanation of this diminution in sensitiveness has been attempted in various directions.

Hargreaves³⁴ believed that there is not a solution of nitrocellulose in nitroglycerine in the nitroglycerine gelatine, but rather a colloidal solution of a definite quantity of nitroglycerine in the nitrocellulose, so mixed with the free, ungelatinized nitroglycerine that the latter is retained in the gelatine by capillarity. He had the idea³⁵ that the ease of detonation and velocity of detonation wave are dependent upon greater or smaller contents of free nitroglycerine. The conception that unchanged, liquid nitroglycerine could be retained by the nitrocellulose-nitroglycerine gel something like a sponge, would be rather difficult to hold. Even the uniformly homogeneous physical structure of the gelatine controverts this. Also, if such were true, even moderate pressures would force out liquid nitroglycerine, but no instance of this is known. Moreover, heating to 75°C. softens the gelatine but it remains uniform. A further result of this conception would be that with a quantity of nitrocellulose which has completely absorbed the nitroglycerine, for example the extreme case of smokeless powder, possibility of detonation must be entirely absent.

As is already known, detonation or sensitiveness of inelastic, horny, nitroglycerine smokeless powders is only a matter of particle size. For example, powder cut in thin plates 2 mm. square, composed of 40 per cent nitroglycerine and 60 per cent nitrocellulose, detonates easily and at a high velocity. Here apparently the air spaces between the powder aggregates, and the increase of surface afford propagation of the wave of detonation.

The air content of fresh blasting gelatine also, as opposed to the Hargreaves conception, has been brought in with apparently more or less justification to explain the ease of detonation and high velocity of

³⁴ *Journ. Soc. Chem. Ind.* (1914), p. 337; *Z. Schiess- u. Sprengstoffw.* (1914), p. 244.

³⁵ *Arms and Explosives* (1911), p. 150.

detonation,³⁶ although it may not form the only explanation of the debated phenomenon.

Freshly mixed blasting gelatine is usually rendered milky by the countless small air bubbles in it. In a vacuum such a gelatine distends from expansion of these bubbles and collapses on releasing the vacuum. After such a treatment a diminution in sensitiveness and lead block expansion is immediately evident.

This air content, which apparently raises the sensitiveness, diminishes gradually on long storage, apparently by the pressure of the mass. The gelatine then becomes denser, clearer and more transparent. Old blasting gelatine is always clear and transparent.

The effect of the air trapped between the particles of an explosive can be illustrated by countless instances. A given explosive, such as trinitrotoluene, detonates easily as a loose, crystalline powder containing air, but much more difficultly as a cast mass containing no air. Liquid ethyl nitrate does not explode when unconfined, but if kieselguhr is mixed with it the lead block is crushed on the ensuing explosion the more so the larger the amount of kieselguhr present, i.e., the more nearly a dry powder or the higher the air content and the less cohesive and plastic it is.

If a blasting gelatine is loosened up by kneading it with some coarse cork powder, or if its cohesiveness is destroyed by a short mixing of the warm, gelatinous mass with 10 per cent kieselguhr to small lumps, the sensitiveness, propagation and velocity of detonation are raised. Such methods are impractical, since they affect the density and total energy, which are important for the special uses of gelatine.

Aside from the trapped air other factors apparently play a part in the diminution of sensitiveness of gelatine explosives, since this phenomenon is very general and is observed in all gelatinous nitroglycerine explosives, even where the enclosed and gradually escaping air bubbles cannot be entirely responsible, as with tough blasting gelatine. It appears that the process of colloid formation is not ended with the process of solution of the collodion cotton, mixing and kneading, and that instead the final state of the colloid in the sense of increase in toughness and consequent reduction in sensitiveness is only reached after some time. This reaction is given the rather unscientific name of "after-gelatinization."

³⁶ Aubert, *Chem. Ztg.* (1913), p. 212.

Blasting gelatine which has become insensitive can again be rendered sensitive by kneading while warm. However, such reworked blasting gelatine becomes insensitive much faster than that freshly prepared, which can be understood if the air content reintroduced by the reworking is not the only cause of the increased sensitiveness of the fresh material. The other causes of the initial state of colloid formation cannot apparently be repeated.

In detonating blasting gelatine a cartridge of guhr dynamite is often used in actual practice as a primer.

Velocity of detonation of blasting gelatine. Just like nitroglycerine, blasting gelatine gives velocities of detonation of far different orders of magnitude. While with liquid nitroglycerine the strength of the initial impulse, confinement and diameter of the train of explosive are the deciding factors as to whether or not the maximum or the characteristic low velocity is developed, with blasting gelatine the influence of the physical condition of the colloid must be added.

The maximum velocity of detonation of blasting gelatine is 8000 meters per second. The values found by various investigators vary considerably, as in all measurements of explosive reactions of very high velocity. Bichel³⁷ found for 92/8 blasting gelatine 7700 meters per second, and Kast³⁸ 7800 m/s for the same composition.

This maximum velocity of detonation, which is developed mainly on close confinement in hard rock, explains, in connection with the high energy content and high density, the extraordinary brisant and shattering effect of blasting gelatine, which is particularly well suited for blasting such rock.

In experiments in iron pipes this velocity is usually found only above a certain diameter, e.g., 30 mm. Moreover, the interesting observation has been made that the velocity only attains its maximum at a certain distance from the point of initiation, then remaining uniform, so that over short stretches, as in short tubes in the Dau-triche method, low values are often obtained. These low velocities, amounting to about 2000 to 2500 m/s, are the rule with small diameters of about 20 to 25 mm. A high content of collodion cotton or increased toughness causes the high velocity to be released more difficultly, so that it is natural for a gelatin difficult to detonate to explode at a lower velocity.

³⁷ Glückauf (1905), p. 465.

³⁸ Spreng- und Zündstoffe, p. 71; *Z. angew. Chem.* (1923), p. 75.

The same thing happens, as is to be expected from the preceding chapter, with gelatine which has been stored for a long time. Storage in warm place (30°C.) for one and one-half years usually gives a velocity of only 1500 m/s in a 25 mm. iron pipe, or below the minimum value, so that such a detonation can no longer be spoken of as brisant, and even the destruction of the pipe corresponds to such a sluggish explosion. Such a gelatine which has been stored too long does not fulfil its rôle in actual practice and causes complaints to the factory.

Gases of explosion. The nitroglycerine molecule contains somewhat more oxygen (3.5 per cent) and the collodion cotton, if enneanitrocellulose or $C_{24}H_{31}N_9O_{33}$, somewhat less oxygen (38.7 per cent) than required for complete combustion to carbon dioxide and water. In the most usual proportions between nitroglycerine and collodion

TABLE 27
Composition of gases of explosion of various blasting gelatines

	BLASTING GELATINE 92/8	SAME WITH 5 PER CENT $KClO_3$	SAME WITH 5 PER CENT $KClO_4$
Expansion of lead block..	595.0 cc.	560.0 cc.	570.0 cc.
Gases, per cent by volume			
CO_2 ...	66.4 per cent	66.5 per cent	66.3 per cent
N_2 ...	33.0 per cent	31.5 per cent	30.9 per cent
O_2 ...	0.6 per cent	2.0 per cent	2.8 per cent

cotton the oxygen excess and deficiency equalize to an almost ideal combustion formula or decomposition equation, which at the same time gives a maximum chemical energy. With 93/7 and 92/8 blasting gelatines there is a small oxygen excess of 0.5 and 0.1 per cent respectively. Bichel³⁹ gives for 93/7 blasting gelatine the following composition of the gases of explosion in per cent by weight: CO_2 61.2 per cent, H_2O 20.3 per cent, N_2 18.1 per cent and O_2 0.4 per cent.

On the other hand, a further increase in the collodion cotton content theoretically leads to the formation of a certain amount of carbon monoxide in the gases, so that in actual practice the combustion of the cartridge paper alters the theoretical decomposition equation in the sense of an increased consumption of oxygen and a certain formation of carbon monoxide.

³⁹ Gluckauf (1904), p. 1043.

In Transvaal therefore, where blasting gelatine is used in large quantities and where poor ventilation is often encountered in the mines, to obtain gases absolutely free from carbon monoxide small quantities (5 per cent) of potassium nitrate, chlorate or perchlorate are added. The product is called anti-fume blasting gelatine. The strength is only changed inappreciably by this slight addition, and the gases are naturally somewhat improved, as the following analyses show:

A collodion cotton with 12.2 per cent N was used, or a mixture of ennea- and decanitrocellulose. The gases were determined by igniting by a glowing platinum wire in an evacuated steel bomb. (See table 27.) For the same reason blasting gelatine is occasionally furnished to Australia for poorly ventilated workings with an appreciable content (20 per cent) of potassium nitrate. However, such an addition lowers the brisance considerably.

According to Kast there can be calculated for 1 kg. of blasting gelatine 710 liters of gases of explosion, corrected to 0°C. and 760 mm.

Heat of explosion; temperature of explosion; strength. On account of the more favorable combustion formula, blasting gelatine gives a somewhat higher development of chemical energy than nitroglycerine. One kilogram of 92/8 blasting gelatine develops 1680 Calories with water as a liquid, and 1560 Calories with water gaseous. For the latter value Bichel gives 1550, Kast 1540 and Heise 1535. Bichel and Heise used a 93/7 composition, Kast a 92/8. Blasting gelatine therefore gives the highest energy of all the practical explosives in use, perhaps with the exception of mixtures of liquid oxygen and carbon, which theoretically could develop an even greater number of calories with an ideal composition, namely about 2200 Calories per kilogram if the composition corresponded exactly to the formula $C + O_2 = CO_2$. In actual practice this is very seldom the case, since with the rapid evaporation of the liquid oxygen the composition of the explosive at the instant of explosion is dependent upon external conditions. The lower energy density of the liquid air mixture does not in general allow it to be so brisant in effect as with blasting gelatine, although under very favorable conditions an effect similar to dynamite is obtained.

The temperature of explosion is given by Heise as 3200°C. Kast⁴⁰ calculates the considerably higher value 4300°C.

The properties depicted correspond to the high strength determined by the ordinary laboratory methods.

Lead block test. Blasting gelatine (92/8) gives about the same

⁴⁰ Spreng- und Zündstoffe, p. 71.

lead block expansion as nitroglycerine when fired in the usual way, or about 560 cc. net. This test also shows clearly the influence of the physical condition or collodion cotton content and the age of the gelatine. Freshly prepared gelatine gives the highest values. The author found with two samples of different collodion cotton contents the net expansions shown in table 28. The tougher gelatine shows a greater drop in brisance even after a few days. With blasting gelatine stored for a longer time the lead block expansion falls to 500 cc. and below. In spite of the favorable proportions of quantity of initiating explosive in a No. 8 cap to the 10-gram cartridge these caps do not then release the highest decomposition velocity.

Camphorated blasting gelatine (87.6 per cent nitroglycerine, 7.6 per cent collodion cotton, 4.8 per cent camphor) naturally gives a somewhat lower expansion. When fresh the author found 555 cc.

TABLE 28

Lead block expansions of blasting gelatines of various ages and collodion cotton contents

	COLLODION COTTON	
	7 per cent	9 per cent
	cc.	cc.
Freshly made.....	600	580
After two days.....	580	545

Lead block crushing. This test also shows clearly the characteristic properties of blasting gelatine. A 93/7 gelatine gave 24.5 mm., a 91/9 gelatine gave 12 mm., both two days old. When detonated unconfined by a No. 8 cap a 100-gram cartridge 400 mm. in diameter in the first case gave apparently the typical high velocity of detonation, in the second the typical low velocity, since this somewhat crude test under uniform conditions shows up simply and clearly the higher or lower velocities of detonation.

Since it was shot without confinement it, at the same time, gives a picture of the sensitiveness. Less sensitive explosives give relatively low crusher tests, but in interpreting this result the energy content, density and lead block expansion must be considered in connection with it.

The above camphorated blasting gelatine gave a crusher test of

24 mm., a sign that a few per cent of camphor does not render the gelatine as insensitive as would be expected from many statements in literature.⁴¹ For the crushing effect on a copper cylinder, shot under confinement, Kast⁴² gives the following comparative values:

	mm.
Blasting gelatine.....	4.8
Nitroglycerine.....	4.6
Gelatine dynamite.....	3.9
Guhr dynamite.....	3.1

⁴¹ Escales, *Nitroglycerin und Dynamit*, p. 246.

⁴² *Spreng- und Zündstoffe*, p. 71.

CHAPTER XXI

GELATINE DYNAMITE

The local shattering action of blasting gelatine, due to its high energy density and velocity of detonation, is not useful everywhere, and it is only of advantage in very tough rock. It was soon attempted, therefore, to graduate the brisant properties of blasting gelatine to suit any given operation by adding materials to the gelatine. Most of such additions consisted of mixtures of wood meal and different kinds of saltpeter, in proportions such that the available oxygen of the nitrate would burn the wood meal completely, while the surrounding gelatine in turn had an almost complete combustion equation.

It is a characteristic that a far "thinner" or softer gelatine, i.e., one having a lower collodion cotton content, forms the basis of these mixtures called "gelatine dynamite," which are very plastic and can be kneaded and shaped, but which are not really elastic or gelatinous in the same sense as the pure blasting gelatine. The wood meal of the mixed absorbent absorbs and retains the nitroglycerine and prevents any exudation.

Assuming a collodion cotton of equal gelatinizing power, a reduction in amount of it in the gelatine causes a rise in velocity of detonation, ease of detonation, propagation, plasticity and flexibility, just as with blasting gelatine, which is important in the preparation of plastic dynamites of low oil content.

The main type of gelatine dynamite most widely used for a long time, and called simply "dynamite" by German miners, contains 65 parts of gelatinized nitroglycerine and 35 parts of the so-called "dope" or absorbent. The collodion cotton content of the gelatine varies between about 2 and 5.4 per cent. The dope consists of about 3 parts of potassium or sodium nitrate and 1 part of wood meal.

¹ In the United States the word dynamite means an explosive containing no collodion cotton, while the word gelatine is used to mean gelatine dynamite and blasting gelatine, very little of the latter being used however.—

TRANSLATOR.

Frequently about 0.2 to 0.35 per cent of prepared chalk is added to neutralize any traces of acid which may be present. The former usual addition of some soda (sodium carbonate) for this purpose, mentioned in many books, must be regarded as impractical, since the strongly alkaline sodium carbonate, in connection with the small quantities of moisture always present and derived from the fresh nitroglycerine and the air-dried wood meal most commonly used, is more suited to attack and saponify the nitroglycerine than to preserve it.

The composition of 65 per cent gelatine dynamite is as follows:

Gelatine.....	{ Nitroglycerine, 63.25 to 61.5 per cent Collodion cotton, 1.75 to 3.5 per cent }	65 per cent
Dope.....	{ Saltpeter 27.0 to 28.0 per cent Wood meal 8.0 to 7.0 per cent }	35 per cent

The quantity of collodion cotton used depends upon its gelatinizing power with nitroglycerine and the special requirements, such as climate, to which the stability of the product must be suited (see Exudation of Blasting Gelatine). In the case of a product for export to hot countries more collodion cotton is usually added. For the so-called gelatine dynamite 1.75 to 2.25 per cent of collodion cotton is the rule.

Climatic conditions also govern the kind of saltpeter used. Although gelatine dynamites, as compared to pulverent dynamites with efficient absorbents, from which they differ only in having the nitroglycerine gelatinized by nitrocellulose, are relatively very insensitive to moisture because the gelatine to a certain extent surrounds the dope and protects the particles of the salt by an impermeable membrane, the hygroscopicity of the saltpeter used comes into consideration in a moist, warm climate. The very hygroscopic Chile or sodium nitrate is customary for German products, which are not often stored very long, particularly in a moist place. Exported goods which have to withstand transportation a month or more, and often long storage in tropical or sub-tropical countries, generally contain the more expensive but non-hygroscopic potassium nitrate.

Some time after the discovery of gelatine dynamite, when ammonium nitrate began to be used as an explosive component, it found use in gelatine dynamites as well, since in spite of being an endother-

mic explosive compound it gives a particularly high strength to explosive mixtures. Due to its great hygroscopicity it was even less suited for export goods than sodium nitrate, and required a special, water-proof packing. Gelatine dynamites containing ammonium nitrate are much used in France. In Germany it is used mainly in permissible gelatine dynamites. Its appreciably higher price than sodium nitrate comes into consideration here.

In place of wood meal, rye flour has been used at times, especially in France and Italy. However, its absorbent power for the gelatine is less than that of wood meal, and it is more expensive.²

In Germany, since the beginning and after the World War, cereal meal and waste meal which are suitable for human food or cattle fodder, have no longer been used for the manufacture of dynamite for obvious reasons.

COMPOSITION OF VARIOUS GELATINE DYNAMITES

In addition to the above basic type, the 65 per cent gelatine dynamite, also called gelignite in England and in some varieties and with slight modifications gelignite in France, in the course of time a large number of gelatine dynamites with various nitroglycerine contents have come into more or less wide use.

In England there was at first often used a gelatine dynamite consisting of 80 per cent nitroglycerine-gelatine and 20 per cent dope, later gradations with 70 to 75 per cent gelatine, and finally almost universally a gelignite almost corresponding to the original type, or 54 to 63 per cent nitroglycerine, 2 to 6 per cent collodion cotton, 24 to 34 per cent saltpeter and 5 to 10 per cent wood meal.³

In France, where a government monopoly of powder and explosives exists and only the nitroglycerine explosives are allowed to be made by private factories, in the course of time countless gradations whose nitroglycerine content varied from 43 to 86 per cent were officially allowed. Escales tabulates them according to their nitroglycerine content in table 29 based on Daniel's *Dictionnaire des matières explo-*

² Cereal meals have been widely used in the United States, mainly on account of their lower absorptive values, which in the case of gelatines rated at 30, 25 and now even 20 per cent strength is very useful because there is then very little oil to absorb.—TRANSLATOR.

³ Daniel, *Dictionnaire des matières explosives*, p. 340.

TABLE 29
Escales tabulation of French nitroglycerine explosives

	GOMME B	GOMME B1	GOMME I	GOMME G	GOMME B2	GOMME MB	GÉLATINE DYNAMITE MB	GOMME C	GOMME D	GÉLATINE	GÉLATINE 1B
Nitroglycerine.....	86.0	85.0	84.0	83.0	82.0	74.0	74.0	70.0	69.5	67.0	64.0
Collodion cotton.....	5.0	5.0	5.0	5.0	6.0	6.0	4.0	4.0	5.5	3.0	3.0
Potassium nitrate.....	4.0	8.0	9.0	10.0	9.0	15.5	11.0	16.0	24.75	20.0	—
Sodium nitrate.....	—	—	—	—	—	—	—	—	—	—	24.0
Wood meal.....	5.0	2.0	2.0	2.0	3.0	4.5	10.5	10.0	0.25	10.0	8.0
Cereal meal.....	—	—	—	—	—	—	—	—	—	—	—
Magnesia.....	—	—	—	—	—	—	0.5	—	—	—	—

	GÉLIGNITE F	GÉLIGNITE F1	DYN. NO. 4	GÉLIGNITE BM	DYNAMITE GÉLATINÉ NO. 1	GÉLATINÉ
Nitroglycerine.....	60.0	60.0	59.0	57.9	57.5	57.0
Collodion cotton.....	3.0	6.0	1.5	2.1	2.5	3.0
Potassium nitrate.....	26.6	23.6	—	—	32.0	34.0
Sodium nitrate.....	—	—	25.0	28.7	—	—
Wood meal.....	10.0	10.4	14.0	—	—	—
Cereal meal.....	—	—	—	11.3	8.0	6.0
Magnesia or soda.....	0.4	—	0.35	—	—	—
Ocher.....	—	—	0.15	—	—	—

	DYNAMITE GÉLATINÉ 2A	GOMME 2	DYNAMITE NO. 5	DYNAMITE GÉLATINÉ 2B	DYNAMITE GÉLATINÉ 2C
Nitroglycerine.....	50.0	49.0	48.0	45.0	43.0
Collodion cotton.....	1.5	2.0	1.0	3.0	2.0
Potassium nitrate.....	42.0	—	—	42.0	41.0
Sodium nitrate.....	—	36.0	36.3	—	—
Wood meal.....	6.5	10.0	14.0	10.0	14.0
Cereal meal.....	—	3.0	—	—	—
Magnesia or soda.....	—	—	0.45	—	—
Ocher.....	—	—	0.25	—	—

sives.⁴ Table 30 gives the French types of ammonia gelatine dynamites. The main gelatine dynamites used in France at the present time are shown in table 31. Of these mixtures the first naturally is very close to pure blasting gelatine as regards physical structure and behaviour, while the second, fourth and sixth do not differ appreci-

TABLE 30
French ammonia gelatine dynamites

	DYNAMITE O	FORCITE EXTRA
	per cent	per cent
Nitroglycerine.....	50.0	64.0
Collodion cotton.....	2.5	3.5
Ammonium nitrate.....	44.5	25.0
Wood meal.....	—	6.5
Cereal meal.....	2.5	—
Magnesia.....	—	1.0
Lampblack.....	0.5	—

TABLE 31
Gelatine dynamites used in France at the present time

	GÉLA- TINE DYNA- MITE (POTASH)	GÉLA- TINE A	GÉLA- TINE B- POTASH	GÉLA- TINE B-SODA	COMME E	GÉLIQ- NITE
Nitroglycerine.....	82-83	64	57.5	57	49	58
Collodion cotton.....	5-6	3	2.5	3	2	2
Potassium nitrate.....	9-10	—	32.0	—	36	58
Sodium nitrate.....	—	24	—	34	—	—
Cellulose.....	2-3	8	8.0	6	13	12
Magnesia.....	—	1	—	—	—	—

ably from the ordinary German gelatine dynamite and English gelignite.

In Belgium, where in general on account of difficult transportation regulations which make shipment of dynamite very expensive, these are very little used, and instead the ammonium nitrate type of explosives is largely made and used. The gelatine dynamite is called

⁴ Escales, *Nitroglycerin und Dynamit*, p. 251.

"Forcite." The composition of the most important is shown in table 32, taken from Escales.⁵

In Austria gelatine dynamites are also called "Neudynamite" and made mainly in the two types shown in table 33, of which the first about corresponds to the German dynamite.⁶

In America gelatine dynamites with 30 to 80 per cent of nitroglycerine are made, but there in addition to these the non-gelatinous,

TABLE 32
Composition of Belgian gelatine dynamites

	FOR- CITE EXTRA	FOR- CITE SUPER- IEURE	SUPER FOR- CITE	FOR- CITE NO. 1	FOR- CITE NO. 1P	FOR- CITE NO. 2	FOR- CITE NO. 2P
Nitroglycerine.....	74	64	64	49	49	36	36
Collodion cotton.....	6	8	3	2	2	3	2
Sodium nitrate.....	—	24	—	36	—	35	—
Potassium nitrate.....	14	—	23	—	37	—	46
Wood meal.....	5	8	9	13	11	11	—
Cereal meal.....	—	—	—	—	—	14	16
Magnesia.....	1	1	1	—	1	1	1

TABLE 33
Composition of Austrian gelatine dynamites

	I	II
Nitroglycerine gelatine.....	66.00	45.00
Saltpeter.....	24.82	40.15
Wood meal.....	8.84	—
Cereal meal.....	—	14.30
Soda.....	0.34	0.55
	100.00	100.00

so-called "straight dynamites" play a considerable rôle.⁷ The dope or absorbent contains, in addition to other things, sulphur, which is

⁵ Escales, *Nitroglycerin und Dynamit*, p. 252.

⁶ Kast, *Spreng- und Zündstoffe*, p. 297.

⁷ The limit should be 20 to 80 per cent instead of 30 to 80 per cent. It is probable that straight dynamites (non-gelatinous), with or without the use of low-freezing liquid explosive components, have played a greater part in the United States than in Europe.—TRANSLATOR.

very cheap in America, but which in underground mining is very likely to form troublesome gases of explosion.⁸ Two analyses of low-strength American gelatine dynamites with 29 to 31 per cent nitroglycerine, 48 to 54 per cent sodium nitrate, starch, wood meal and sulphur are given by Hall and Howell.⁹

In Germany for years large amounts of the above-mentioned 65 per cent gelatine dynamite have been made and used. In addition to this, large quantities have been exported to the English colonies, mainly Transvaal and Australia, to Japan and many other foreign countries overseas, containing potassium nitrate instead of sodium nitrate.

The dope or absorbent for domestic products consists of 76.9 per cent sodium nitrate, 22.6 per cent wood meal and 0.5 per cent of chalk, that for export contains 80 per cent potassium nitrate, 19.5 per cent wood meal and 0.5 per cent chalk, thus containing somewhat more saltpeter than Chile saltpeter, since the former contains less available oxygen on account of the higher atomic weight of the potassium than does the sodium nitrate, or 39.6 per cent versus 47 per cent.

For certain purposes a weaker, so-called Gclignite II, containing 47.5 per cent nitroglycerine, 2.5 per cent collodion cotton, 37.5 per cent potassium nitrate, 3.5 per cent wood meal and 9 per cent rye meal is exported.

On the other hand, high strength gelatine dynamites of the composition given in table 34 are made for export. Formerly weaker types were mainly used in Germany, containing 53.5 per cent nitroglycerine, 1.5 per cent collodion cotton and 45 per cent absorbents of the above composition with sodium nitrate, or a 55 per cent gelatine dynamite.

The World War, with its scarcity of glycerine, caused a fundamental change along the line of utilization of gelatine dynamites containing a lower per cent of nitroglycerine, which taught economy

⁸ At present the evidence seems to be that the gases of explosion obtained in actual underground use of gelatine dynamites containing sulphur do not contain sulphurous gases, all of the sulphur going to form sulphates with the sodium, but if tested in the Bichel Gauge large quantities of sulphurous gases are obtained, due to lack of confinement on detonation and different reactions.

—TRANSLATOR.

⁹ *Bur. of Mines Bull.* 59 (1913), also *Z. Schiess- u. Sprengstoffw.*, (1917), p. 250.

and limitation in all fields. Since this time, when glycerine was first confiscated and then released, with a rise in price, the consumption of 65 per cent dynamite has fallen off, and it is now used only where absolutely necessary and where blasting with a weaker explosive is impossible or uneconomical, while many places formerly using 65 per cent dynamite have now learned to use a 40 per cent dynamite. This product is often improperly called "Substitute Dynamite." Although it naturally has a lower energy content than the higher strength dynamite with 65 per cent of gelatinized nitroglycerine, it still has the characteristics of gelatine dynamite, such as high density, high velocity of detonation and good plasticity. The explosive character of the nitroglycerine in it is exerted completely, in contrast to even the strongest of the ammonium nitrate dynamites, which in

TABLE 34
Composition of German high strength gelatine dynamites

	80 PER CENT	81 PER CENT	75 PER CENT
	per cent	per cent	per cent
Nitroglycerine.....	75	75.8	70.4
Collodion cotton.....	5	5.2	4.6
Potassium nitrate.....	15	15.2	19.3
Wood meal and some chalk.....	5	3.8	5.7
	100	100.0	100.0

spite of their greater total energy cannot be used in hard ore or rock to compete with even the lower strength gelatine dynamites on account of their lower velocity of detonation and lower density.

In such low strength dynamites the customary dope or absorbent of saltpeter and wood meal proportioned so as to give complete combustion, cannot be maintained, since the wood meal content would then become so high that an explosive sufficiently plastic to cartridge well could not be made. The result is a relatively high saltpeter content and consequently an excess of available, unused oxygen. Since the saltpeter not used for combustion of the explosive does not increase the strength of the latter, and does not act much differently than any salt not taking part in the decomposition, often a part of the excess saltpeter is replaced by any cheap, neutral salt such as common salt, which then plays only the part of a ballast or filler.

This suggests the idea that such a process must be irrational, since the miner instead of using the cheaper, low-strength dynamite with inert fillers, could just as well or even better use a correspondingly smaller quantity of the more expensive but stronger high-strength dynamite. However, this does not appear to be the case. Moreover, any mercantile point of view of the factory, which could perhaps find an advantage in the greater sale of the weaker, cheaper dynamite would not have been able to carry on long. As a matter of fact, it seems that the "stretched" dynamite in many cases is particularly advantageous and economical, perhaps because in many kinds of rock the distribution of the same amount of energy over a larger surface is more effective as regards results in blasting than the accumulation or concentration of the energy in a smaller space, or because formerly unnecessarily great amounts of energy were used. Under the influence of present conditions economy is watched to a greater degree than formerly and the cheaper, lower strength dynamites are now adopted where they are sufficient and where formerly they could have been used.

Moreover, attempts have been made in the low strength dynamites to replace the voluminous wood meal wholly or in part by other, heavier carbonaceous materials as consumers of the oxygen of the saltpeter without desensitizing the nitroglycerine, i.e., without affecting its physical condition so as to diminish the velocity of detonation. Such materials are mainly the well known aromatic nitrocompounds which are used as explosive components of ammonium nitrate and chlorate explosives, such as trinitrotoluene and dinitrotoluene, which are in themselves explosives and which desensitize the nitroglycerine very little although they partly dissolve in it.

By replacing saltpeter by potassium perchlorate, which is not much used on account of its high price, effects can be obtained with a dynamite having a low per cent of nitroglycerine which correspond to those having a high per cent of nitroglycerine and saltpeter. The potassium perchlorate furnishes just as much oxygen (46.2 per cent) as sodium nitrate (47 per cent), decomposes more easily and is denser, so that it increases the density of an explosive. Thus a 40 per cent dynamite containing potassium perchlorate, in which the wood meal has been partly replaced by hydrocarbons such as naphthaline, has a particularly good effect.

Reduction of the nitroglycerine content has been carried down to 18 per cent, and during the war a so-called 18 per cent substitute dynamite, a plastic, gelatinous explosive of a nature more like dynamite and having a very effective action was supplied. It contained only 18 to 20 per cent nitroglycerine. In order to be able to work up an explosive containing so little nitroglycerine-gelatine to a plastic mass in the usual way which could be cartridged, it is necessary to "stretch" or "extend" the gelatine, as it is called in the explosives plants. This is done by the above-mentioned addition of aromatic nitrocompounds, which partly dissolve in the nitroglycerine.

An oxidizing material as heavy as possible, such as potassium perchlorate, is of advantage in such "stretched" gelatines or dynamites with a low nitroglycerine content, in order to obtain a high plasticity and high brisance.

Recently the sale of mining explosives in Prussia has been subjected to a new regulation by a police order of January 25, 1923, taking effect January 1, 1924, with the idea of making it more uniform. It is assumed that this uniformity will be extended to the whole country in a reasonable time. The regulation, which governs the designation and composition of explosives permitted by the administration and determines their field of use, i.e., divides them into explosives for rock or ore and explosives permitted in gaseous and dusty mines, applies only to those operations subject to police inspection by the mining authorities, but it is expected that in the course of time the field of application will be extended to all civil, commercial uses of explosives.

According to the first list of mining explosives of February 1, 1923¹⁰ the kinds of dynamite listed in table 35 may be sold to Prussian mines in the future from plants specially authorized.

Ammonia gelatine, a more gelatinous, safer to handle and non-freezing explosive containing mainly dinitrochlorohydrine with a maximum of 5 per cent nitroglycerine, is also admitted under the group Dynamite. It will be considered in the next chapter, under non-freezing nitroglycerine explosives.

Of these five kinds of dynamite, dynamite 1 represents the old 65 per cent gelatine dynamite, with the possibility of replacement of the sodium nitrate either wholly or in part by potassium perchlorate.

¹⁰ *Deutscher Reichsanzeiger und Preussischer Staatsanzeiger No. 41, February 17, 1923, Erste Beilage.*

TABLE 35

Dynamites which may be sold legally in Prussian mines

	DYNAMITE 1	DYNAMITE 2
	per cent	per cent
Nitroglycerine.....	61.0-63.5	56.0-61.0
Collodion cotton.....	1.5- 4.0	—
Nitrocellulose.....	—	4.9- 9.0
Sodium nitrate and/or potassium perchlorate.....	25.0-29.0	—
Wood meal.....	6.0- 9.0	3.0- 8.0
Soda and/or chalk and/or harmless colors like ocher, caput mortuum.....	0.0- 2.0	—
Nitrocompounds from toluene and/or naphthaline and/or diphenylamine.....	—	0.0- 4.0
Alkali nitrate and/or potassium perchlorate.....	—	25.0-30.0

	DYNAMITE 3		DYNAMITE 4
	per cent		per cent
Nitroglycerine.....	34.0-39.0	Nitroglycerine.....	36.0-39.5
Nitrocellulose.....	1.0- 6.0	Nitrocellulose.....	0.5- 4.0
Vegetable meal.....	1.0- 6.0	Vegetable meal and/ or solid hydrocarbons....	1.0- 7.0
Nitrocompounds of toluene and/or naphthaline and/or diphenylamine.....	6.0-10.0	Alkali nitrates and/ or ammonium nitrate and/ or potassium perchlorate.....	40.0-50.0
Alkali nitrates and/or ammonium nitrate and/or potassium perchlorate.....	44.0-54.0	Inorganic inert salts.....	7-12

	DYNAMITE 5		BLASTING GELATINE
	per cent		per cent
Nitroglycerine.....	16.0-20.0	Nitroglycerine.....	92.0-94.0
Collodion cotton.....	0.5- 2.0	Collodion cotton.....	8.0- 6.0
Potassium perchlorate and/ or ammonium nitrate and/ or alkali nitrate....	50.0-74.0		
Nitrocompounds of toluene and/ or naphthaline and/ or diphenylamine.....	2.0-12.0		
Vegetable meal and/or solid hydrocarbons.....	1.0- 6.0		
Alkali chloride	0.0-12.0		

Dynamite 2 is of the same type and presents the possibility of working into these limits semi-finished smokeless powder which is still obtainable from the army stocks, i.e., gelatinizing the nitroglycerine with a corresponding quantity of this semi-finished mass, instead of with collodion cotton, since the former always contains soluble nitrocellulose. Semi-finished smokeless powder with 40 per cent nitroglycerine can be added up to 15 per cent, according to quality.

Dynamites 3 and 4 refer to the 40 per cent gelatine dynamite mentioned above, much used in recent times, also offering the possibility of replacement of collodion cotton by semi-finished smokeless powder. Dynamite 3 also allows as carbonaceous ingredients aromatic nitrocompounds in addition to vegetable meal. In addition to wood meal, vegetable meal also embraces heavy vegetable meals such as tumeric meal and "Olmedo" meal, as well as the residue from wood spirit manufacture. The main representatives of the nitrocompounds are di- and trinitrotoluene, in addition to dinitronaphthaline, trinitronaphthaline and hexanitrondiphenylamine, obtained from the army stores.

Dynamite 4 provides for solid hydrocarbons instead of nitrocompounds in addition to or in place of vegetable meals, such as naphthaline and anthracene, as well as the ballast or filler mentioned. Finally, dynamite 5 represents the so-called 18 per cent gelatine dynamite previously mentioned, always containing a considerable quantity of nitrocompounds to stretch out the nitroglycerine content.

MANUFACTURE OF GELATINE DYNAMITE

Preliminary preparation of the "dope"

Since the dope usually consists of oxidizing agents such as salt-peters or perchlorates on the one hand and combustible ingredients such as wood meal, cereal meal, powdered coal, etc., on the other hand, it is important for the most rapid and complete combustion or participation in the instantaneous decomposition to mix the various constituents in as finely pulverized a condition as possible and as intimately as possible.

On the other hand, they should also serve as absorbents or at least assist the retention of the nitroglycerine. It can easily be realized that substances of a dense structure, such as salt crystals, charcoal and anthracite coal, have a greater retentive capacity in a

finely divided form than in coarse particles. Wood meal must not be too finely divided if it is not to suffer in absorptive capacity. It is usually furnished in a sufficiently fine condition, and it is only necessary to put it through a shaker screen with 1 to 2 mm. openings to free it from the coarser particles and foreign bodies. Today it is frequently used in an air-dried condition, with 8 to 10 per cent moisture, since experience has shown that the small quantity of moisture so introduced into the explosive does not affect the properties and effectiveness of nitroglycerine explosives. Where this is not done it is given a preliminary drying in kilns or steam-heated driers, and occasionally the meal is also dried at 100 to 120°C. on flat, sheet iron plates which can be pushed into the drying chamber on rails and so undergoing a light roasting, which is said to increase the combustibility.

The anthracite coal or charcoal, occasionally used, is ground to a fine powder in an iron ball mill with iron balls by sufficiently long grinding, a moderate charge in the mill being of advantage.

Nitrocompounds, such as trinitrotoluene, usually furnished in a granulated condition, in flakes or scales, are ground to a fine powder in a wooden edge mill. Under certain conditions, such as with soft nitrocompound mixtures of low crystallizing point a preliminary mixing of these with the other constituents of the dope, wood meal and saltpeter, on heated plates can be done, the nitrocompounds melting and mixing intimately with the other constituents.

Potassium perchlorate should not be put under rolls, because here there is always friction and pressure due to the revolving copper rolls and the metal scraper which give the mixing action. Perchlorates in admixture with the organic components of the dope form brisant explosives, sensitive to friction and not safe to handle.

Nitrocompounds of low melting point, such as commercial dinitrotoluene, the so-called drip oil or *m*-dinitrotoluene, a mixture of isomeric dinitrotoluenes consisting mainly of *m*-dinitrotoluene, and nitronaphthalene, can be melted and dissolved in the nitroglycerine instead of being mixed with the components of the dope, and gelatinized in the gelatinizing pan. Like nitroglycerine, they gelatinize with collodion cotton, as is well known.

As regards specifications for the nitrocompounds it should be mentioned that they must be absolutely free from mineral acids. They are usually tested by boiling about 50 grams in a flask with 100 cc. of

water for ten minutes. After cooling they are filtered and the filtrate titrated with N/10 caustic alkali. The acid found should not be more than 0.1 per cent of the nitrocompounds, calculated as HNO_3 . The low acid content found in well purified, commercial nitrocompounds consists of small quantities of weak organic acids, which involve no risk.

Saltpeter and salts are given a preliminary drying on steam-heated, circular pans, the above-mentioned roller drier, or in other special driers, and ground to a fine powder in a Gruson or Excelsior mill. In the case of salts such as alkali chlorides, which serve as a ballast or filler, fine grinding is not necessary, since they do not take part in the decomposition. On the contrary, fine grinding of considerable percentages of such a ballast material is even a disadvantage, since they naturally hinder the passage of the wave of detonation the more the greater their surface. It is sufficient to screen such salts to free them from coarse particles.

Potassium perchlorate is usually supplied as a fine crystal meal and therefore requires no special grinding. Since it is not hygroscopic and usually contains only 0.04 to 0.05 per cent moisture, further drying is superfluous. In case it occurs in coarse crystals it may be ground in an iron barrel or Excelsior mill only if all organic contamination of the product or the mill is absolutely excluded, since in admixture with even very small quantities of organic substances it becomes an explosive and can then be readily ignited or exploded by shock or friction. Potassium perchlorate which has been recovered from munitions by extraction with hot water usually contains a few per cent of aromatic nitrocompounds as impurities unless it has been subjected to a special purification with organic solvents, and in this condition it is an explosive sensitive to shock and friction, although giving a low effect. Such potassium perchlorate should only be ground in a wooden drum with wooden balls or in a wooden edge mill.

The previously mentioned police order of January 25, 1923 prescribes in section 12 that potassium perchlorate, as it comes from munitions, may contain up to 1.5 per cent dinitrobenzene.¹¹

¹¹ According to a recent provision of the Minister of Commerce and Labor dated June 29, 1923, 3 per cent dinitrobenzene in potassium perchlorate is allowed.

The components of the dope, prepared as above, with the exception of the perchlorate which is only added to the mixer, are subjected to a thorough mixing in a mixing drum with *lignum-vitae* balls. Dope so mixed is stored in heavy linen sacks or in covered sheet iron barrels, but is usually used fresh, since if it contains hygroscopic materials such as sodium nitrate or ammonium nitrate it can very easily absorb moisture. Although the dope is not an explosive mixture like black powder in the true sense of the word, it is very combustible, and fires occur occasionally in the mixers. It is therefore advantageous to construct these buildings as nearly fireproof as possible, to isolate the different divisions by stone walls and to construct the roof of iron or incombustible materials.

Manufacture of Dynamite

The process of manufacture, preliminary gelatinization or gelatinization and mixing, corresponds exactly to the manufacture of blasting gelatine described in the previous chapter, and is done in the same rooms and with the same apparatus. If the preliminary gelatinization is done cold in boxes the dope is added to the mixing machine. In the case of the English gelignite it is customary not to prepare the dope separately but to add saltpeter and wood meal to the mixing machine, which gives a sufficient mixing with the particularly long time of mixing given in the heated English mixing machines.

On the other hand, if pre-gelatinization is done in copper pans heated by warm water there is given a so-called "pre-mixing" by hand of the dope with this thin gelatine for twenty to thirty minutes, then the semi-finished mass is put into wooden troughs and taken to the mixing house, where it is given a further mixing in Werner-Pfleiderer machines for 10 to 15 minutes to form the gelatine dynamite. The finished, plastic mass is then taken in the same wooden troughs to the cartridge house, where it is packed into cartridges in the same way and with the same machines as with blasting gelatine.

It should be noted that the dope must be rubbed through a 2 to 4 mm. mesh screen having a wooden frame by a wooden paddle¹² just before use, preferably in a special room, in order to free it from any foreign bodies which would be a source of danger during the mixing. The occasional practice of locating the screen above the gelatinizing

¹² Revolving brushes are used in the United States.—TRANSLATOR.

pans and screening into the latter directly is not recommended, because it can give rise to dangerous shocks of the heavy screen or friction of the latter on the edges of the pan, which are covered with collodion cotton dust and particles of gelatine.

The cartridge paper is parchment, or most frequently today the cheaper paraffined paper.¹³ The packing is described under guhr dynamite and blasting gelatine. In order to protect the package from moisture on long storage or wetness it is often immersed in hot paraffine.

A particularly good mixing and kneading machine for the manufacture of gelatine dynamite has been built for some time by the Draiswerke G. m. b. H. in Mannheim-Waldhof. This so-called "Column Mixing Machine" has the vertical mixing shafts and removable bowl like the English mixing machine described in the section on blasting gelatine, but it differs from it in the form of the mixing blades, which resemble those of the Werner-Pfleiderer machine and which make possible a much more rapid mixing of the mass than is possible with the finger-shaped blades of the English machine. The main advantage of the Draiswerke design (figs. 34 and 35) is that a pre-mixing of the gelatine with the dope in the gelatinizing pan, transfer and transportation of the semi-finished mass to the mixing house is avoided, and gelatinization, pre-mixing and kneading are done in one and the same apparatus in the same building.¹⁴

The cylindrical, double-walled mixing bowl, which can be connected to warm water pipes so that the hollow wall can be filled with water at the desired temperature, is easily moved on ball-bearing wheels and guide rails. For each mixer a series of such bowls are provided, the latter serving at the same time as gelatinizing pans.

They have a total capacity of 290 liters, so that they easily hold 200 kg. (484 pounds) of gelatine dynamite. They are of brass on the inside and wrought iron on the outside. The exterior wall of the bowl is covered with a wood or linoleum jacket.

As soon as the nitroglycerine is sufficiently gelatinized the dope is shaken in, the bowl pushed in under the mixing frame and the stirrers let down. The latter are raised and lowered by a hand crank, but if desired this can be arranged to be automatic through a friction drive. The cover of the mixing bowl, which rises and falls with the stirrers,

¹³ Paraffined paper is universally used in the United States.—TRANSLATOR.

¹⁴ This is also true of American practice.—TRANSLATOR.

is of oak and linoleum. Points of impact of the stirrer cross bar on the column are covered with vulcanized fibre. All chains on the machine are of steel, the pulleys of gray cast iron. All wheels and spindles on which the stirrers move up and down are well covered. The base plate is channeled for the wheel tracks and so arranged that the brass rollers do not touch iron. The agitator shaft and blades are cast out of a single piece of bronze.

An absolutely homogeneous mixing of the mass requires only eight to ten minutes in this apparatus. The power consumption varies from 6 to 12 H. P.

The combining of pre-gelatinization, pre-mixing and mixing in one vessel in the same room gives a saving in labor. The whole process is characterized by simplicity and cleanliness. Another advantage is that the bearings of the mixing arms are not in contact with the mass of the explosive, as in the case of the Werner-Pfeiderer machine, so that there is no question here of penetration of the mass into the bearings, hardening there, and consequent friction.

Preparation of small samples of gelatine dynamite in the laboratory

For example, 100 to 200 grams composition as follows:

	<i>per cent</i>
Nitroglycerine.....	62.5
Collodion cotton.....	2.5
Saltpeter.....	27.0
Wood meal.....	8.0

For gelatinization it is best to use a small porcelain casserole with a handle, in which 125 grams, for example, of cold nitroglycerine is weighed, and 5 grams of finely screened collodion cotton well mixed with the cold oil. The casserole is then placed on a water bath at 60 to 65°C. and this temperature maintained by a small flame. After about twenty minutes gelatinization takes place, the gelatine then having the consistency of a thick syrup. Meanwhile 54 grams of saltpeter and 16 grams of wood meal have been intimately mixed in a porcelain mortar, and this dope is then gradually added to the thin gelatine while vigorously stirring with a horn spatula. After all of it has been added the mass is kneaded with the fingers like bread dough. Since most people quickly develop a headache in this operation, even when washing the hands with acetone immediately after, it

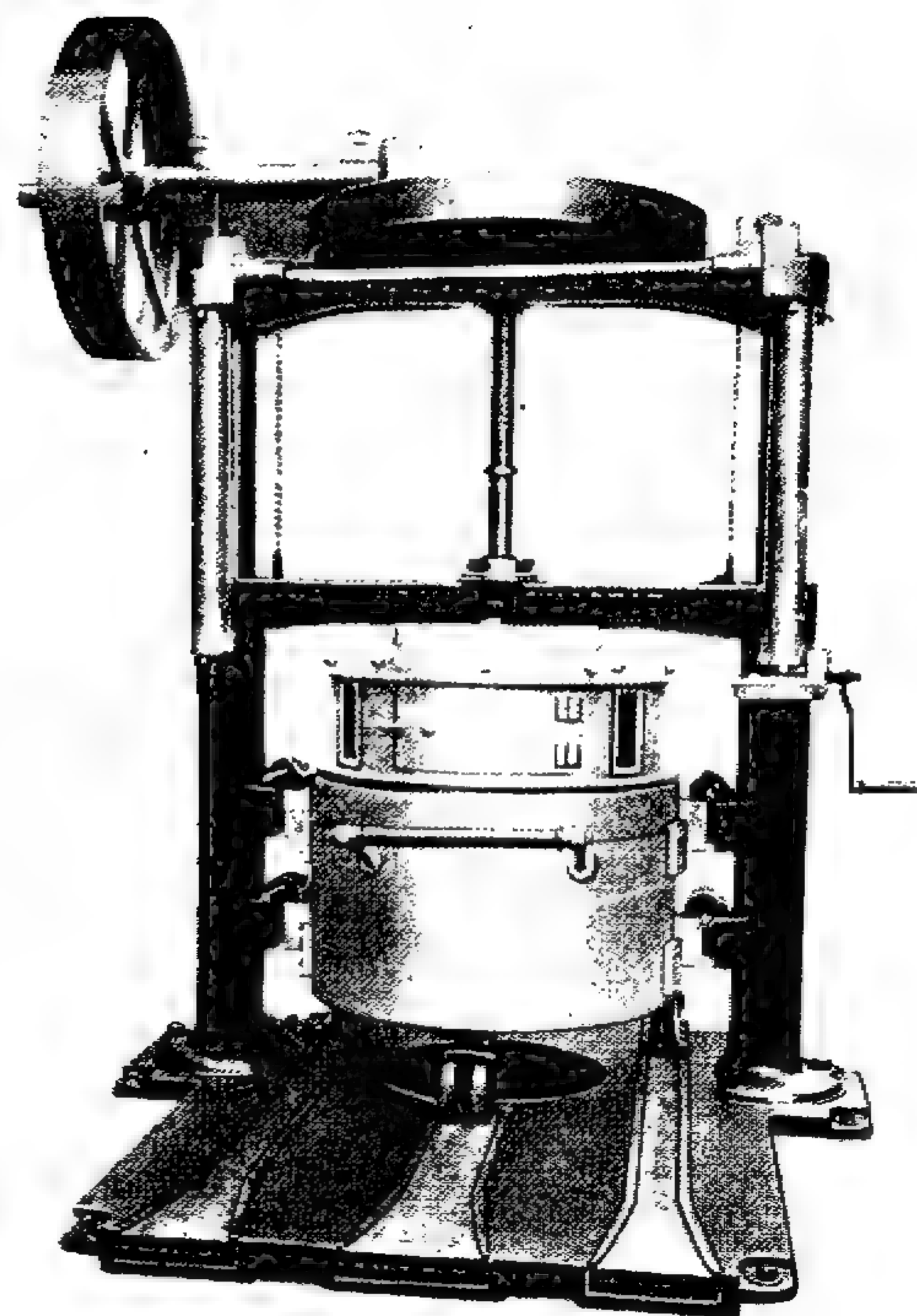


FIG. 34. GELATINE MIXING MACHINE

is recommended that the thorough mixing to complete homogeneity be done in a wooden mortar with a wooden pestle. The homogeneous paste is rolled out into a string or sausage on a board, the sausage cut by a horn spatula into suitable lengths, which are rolled in cartridge paper.

Small residues of dynamite are dissolved in acetone, the acetone solution absorbed in wood meal or dope, and the mixture immediately burned on a metal plate.

PROPERTIES AND STRENGTHS OF GELATINE DYNAMITES

Plasticity

In an unfrozen condition gelatine dynamites are cohesive, plastic masses which can be kneaded and shaped. When they have a high nitroglycerine content they approach the gelatinous nature of pure blasting gelatine and are then less plastic but very elastic. The degree of plasticity is dependent upon the collodion cotton content of the gelatine and the gelatinizing power of the collodion cotton, and also upon the nature of the other components, such as wood meal and oxidizing salts. Gelatine dynamite to be commercially useful should be so soft, flexible and plastic that it can be pressed into a sausage-like shape by the worm cartridging machine described under blasting gelatine, without any particular trouble or exertion of force.

Density

Gelatine dynamites are characterized by a particularly high density, as compared to most pulverent dynamites. This density varies from about 1.5 to 1.8, depending upon the quantity of gelatinized nitroglycerine and content and nature of the salts and carbonaceous ingredients. Ordinary 65 per cent gelatine dynamite has a density of 1.52 to 1.55. The 40 per cent dynamite containing trinitrotoluene and sodium nitrate 1.63 to 1.65, 40 per cent dynamite with high percentages of saltpeter and salts about 1.7, and those containing potassium perchlorate 1.8 and higher, the so-called 18 per cent dynamite (No. 5 of the new Prussian Police Order) with potassium perchlorate likewise about 1.8, and that containing ammonium nitrate only about 1.6.

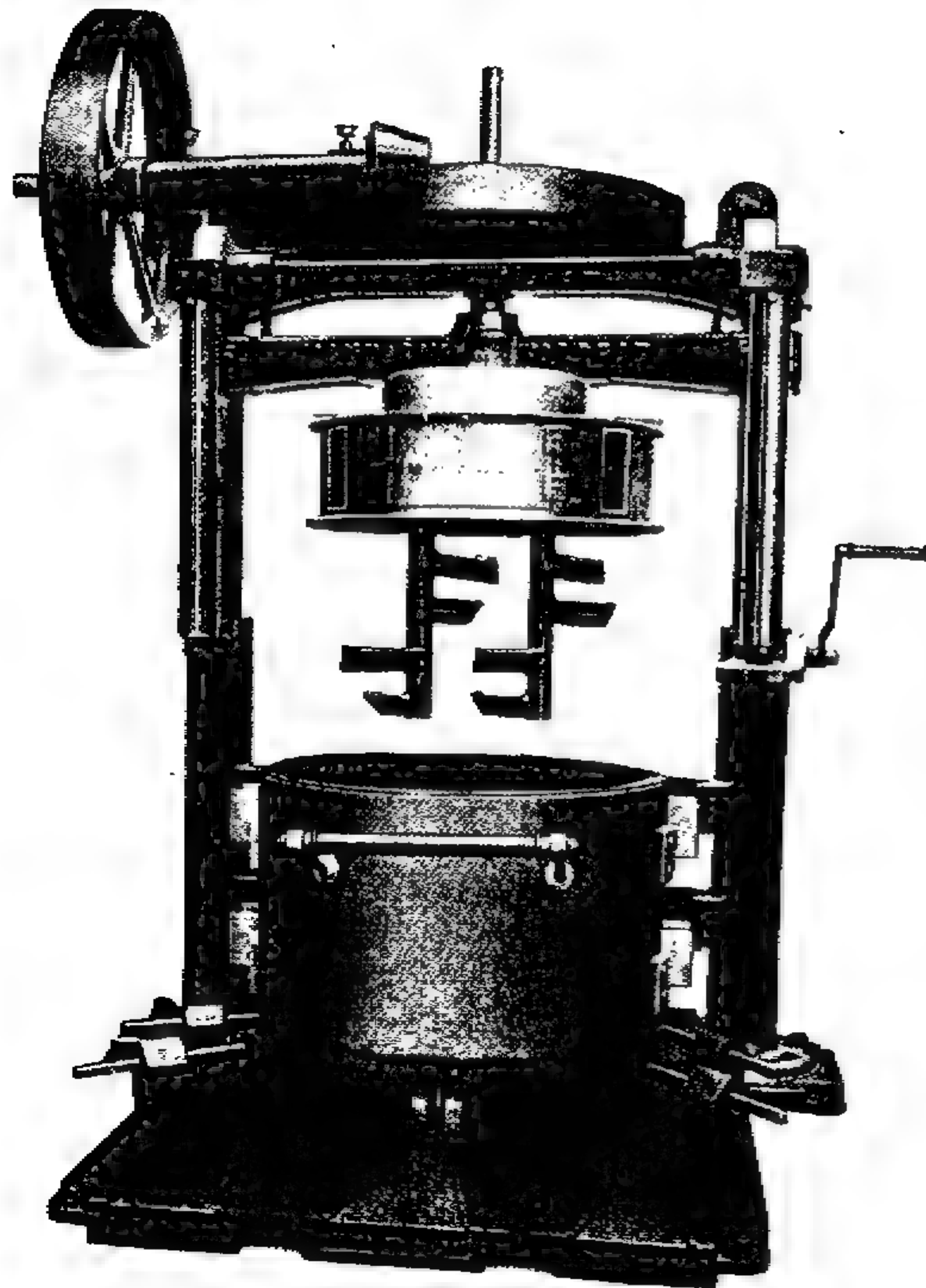


FIG. 35. GELATINE MIXING MACHINE

Stability

Gelatine dynamites should exude no liquid nitroglycerine even on long storage or at gentle heat. As regards exudation the same thing applies here as with blasting gelatine, for example the cartridge paper should not become greasy in twenty-four hours at 40°C. and after this period the mass should separate from the paper easily. After eight days at 30°C. no nitroglycerine should exude. The degree of fulfilment of these conditions depends upon the quantity and degree of gelatinizing power of the collodion cotton.

Gelatine dynamites are relatively stable toward moisture, the more so the higher their content of gelatinized nitroglycerine. However, the nature of the salts contained in the dope plays an appreciable rôle, so that for products intended for tropical countries non-hygroscopic salts such as potassium nitrate, potassium perchlorate, etc., are used almost exclusively.

With dynamites containing lower percentages of nitroglycerine-gelatine and particularly hygroscopic salts such as ammonium nitrate, for this reason a special, water-proof packing, called carton packing, is often used, i.e., the cartridges wrapped in paraffined paper are placed in small paper cartons containing 1 to 1.25 kg. (2½ to 2¾ pounds) which are also dipped into paraffine, then two of the latter are packed into a larger paper carton, which is in turn wrapped in paper and dipped into melted paraffine.

Chemical stability. The same thing applies here as with blasting gelatine. The Abel Test is made in the same way by mixing with talc. Gelatine dynamite made from perfect raw materials as a rule gives no reaction within twenty minutes. English regulations require ten minutes. The German railway regulations require heating for forty-eight hours of whole cartridges at 75°C. without evolution of visible decomposition products.

Sensitiveness to shock and blows. The sensitiveness of gelatine dynamite to blows is not appreciably different from that of blasting gelatine and guhr dynamite. According to Will 65 per cent gelatine dynamite detonates with the 2 kg. falling weight at 17 cm. Lenze occasionally obtained explosion at 5 and 10 cm. drops.

Here also the toughness of the gelatine is not without influence in that the stiffer gelatine dynamites with the higher collodion cotton contents are less sensitive than those with the thinner gelatine. The

author, with a 65 per cent export dynamite containing 3.5 per cent collodion cotton and potassium nitrate, only obtained explosion with the 2 kg. weight at drops of 25 to 30 cm. Potassium perchlorate raises the sensitiveness to shock as compared with potassium nitrate. If the nitroglycerine is desensitized, for example by aromatic nitro-compounds, the sensitiveness to shock is reduced considerably. Gelatine dynamite which has become moist is less sensitive to shock than when dry.

Freezing properties. Gelatine dynamite freezes very readily, usually more easily than blasting gelatine, forming a stiff, hard mass, which only thaws gradually above 13°C. In a frozen condition it is less sensitive to shock and always difficult to detonate.¹⁵

Ignition; explosion by heating. Here also there is a perfect analogy with all nitroglycerine explosives. Gelatine dynamite is easily ignited by contact with a flame, and burns vigorously with a hissing sound. When in large quantities combustion can easily pass into detonation. The explosion point on heating small samples in the usual way in a beaker (20° per minute) is 204 to 205°C., as with blasting gelatine. Heating to high temperatures always causes detonation. Above 180° there is decomposition and evolution of red vapors in increasing quantities.

Sensitiveness to detonation by initial impulse; propagation of detonation. The statement made in the chapter on blasting gelatine on the sensitiveness of gelatinous explosives to an initial impulse naturally applies also to gelatine dynamites, which, however, are in general easier to initiate and which propagate detonation better than pure blasting gelatine, mainly due to their relatively lower content of collodion cotton but also to the breaking up of the colloidal mass by the intermediate dope, mainly the loose wood meal. The toughness of the gelatine, and so the content of collodion cotton, is the governing factor.

The appearance of physical changes such as diminution of ease of detonation, propagation of detonation and velocity of detonation on long storage, particularly at elevated temperatures, three characteristics which in one and the same type of explosive are closely related, applies to gelatine dynamite in almost the same degree as to

¹⁵ Except for special orders gelatine (dynamite) in the United States is always made with low-freezing or non-freezing ingredients.—TRANSLATOR.

blasting gelatine, only with the difference that they become more perceptible with the higher collodion cotton contents such as must be used for export goods, for example with 65 per cent gelatine dynamite containing 3 to 3.5 per cent collodion cotton. The domestic gelatine dynamites, which can usually be consumed more quickly, and in which exudation is not criticized so severely as in the English colonies, for example, with their lower collodion cotton content of about 1.7 to 2.0 per cent in the 65 per cent gelatine, 1 per cent in the 40 per cent and 0.7 to 0.8 per cent in the 20 per cent nitroglycerine-gelatine, do not have their properties noticeably affected by such a change in condition. They always detonate uniformly with the weakest ordinary blasting cap, a No. 1, and in the open propagate detonation to considerable distances, the latter being naturally dependent upon weight and diameter of the cartridge.

The most common cartridge diameters of gelatine dynamite are 23 and 25 mm., but 22, 20 and even 18 mm. are frequently used. These sizes would be 0.9, 1.0, 0.87, 0.79 and 0.71 inches respectively.¹⁶

A cartridge of 65 per cent gelatine dynamite containing 2 per cent collodion cotton, 12 cm. ($4\frac{3}{4}$ inches) long and 25 mm. (1 inch) in diameter, propagates detonation to a similar cartridge 10 to 12 cm. (4 to $4\frac{3}{4}$ inches) away. Even the weaker 40 and 20 per cent dynamites as a rule have a striking ease of detonation and propagation, for example 5 to 8 cm. (2 to 3 inches) with a No. 1 cap.¹⁷

The occurrence of this so-called propagation in the open and its maximum distance is the factory control of each mixing of explosives, and is the most useful criterion of a sufficient sensitiveness to detonation for practical use.

For the miner the question of greater sensitiveness is at the same time one of cost, since with a dynamite of greater sensitiveness he can use a weaker blasting cap, which is considerably cheaper. He is accustomed to use a No. 3 cap with gelatine dynamite, while with the ammonium nitrate safety explosives a No. 8 cap is commonly used.

Gelatine dynamite with a high collodion cotton content (for export goods) requires a stronger blasting cap, especially after long and hot storage. A 65 per cent dynamite with 3.5 per cent collodion

¹⁶ Cartridges as large as $5\frac{1}{2}$ to 6 inches by 16 to 18 inches have a large sale in the United States for use in large holes in quarries.—TRANSLATOR.

¹⁷ No blasting caps smaller than No. 6 are made in the United States. Propagation or gap tests are required to be much greater here.—TRANSLATOR.

cotton, which showed propagation when fresh with a No. 3 cap, after storing for several months at 30°C. required No. 7 or 8 caps. Moreover, the toughness of the gelatine, as well as the nature of the oxidizing salts, is of particular influence upon the sensitiveness to detonation of the gelatine dynamite. The perchlorates, for example ammonium perchlorate which is little used on account of its high price, which give up their oxygen more readily than the sluggish alkali nitrates, have a favorable influence upon the sensitiveness to detonation of gelatine dynamites, which with dynamites high in collodion cotton can equalize the disadvantage of long storage, and with low strength dynamites in which the nitroglycerine is "stretched" and desensitized by aromatic nitrocompounds can counteract such a desensitizing action and ensure a satisfactory sensitiveness and propagation to such mixtures. This fact is explained by the lower heat of formation of the perchlorates, which under equal conditions give a higher heat of explosion, a higher temperature of explosion and higher explosion pressures than the alkali nitrates, all of which is naturally favorable to propagation of detonation.

*Velocity of detonation of gelatine dynamite.*¹⁸ With regard to the velocity of detonation of gelatine dynamite there is a condition analogous to that of blasting gelatine. The gelatinous basis governs the velocity developed, even with the low strength dynamites, although the nature of the other components, especially the oxidizing agents, is not wholly without influence. This influence extends more to the degree of ease with which the maximum velocity of detonation is released, which is of about the same order of magnitude in all types of gelatine dynamites, amounting to about 6500 meters per second, and which is determined only by the character of the nitroglycerine.

With gelatine dynamite also, strikingly low velocities of detonation are obtained at times, amounting to 2000 to 2500 meters per second,¹⁹ and here the same factors as with blasting gelatine, namely collodion cotton content and toughness of the gelatine, diameter of the explosive train and degree of confinement, play an important rôle.

The rise in velocity with increasing distances from the cap in the

¹⁸ Stettbacher, *Schiess- und Sprengstoffe*, p. 48, 133, 139; Kast, *Spreng- und Zündstoffe*, p. 71; Escales, *Nitroglycerin und Dynamit*, p. 256.

¹⁹ Usually obtained with gelatines containing 20 to 35 per cent low freezing explosive oil mixtures.—TRANSLATOR.

Dautriche test in an iron pipe, especially with small diameters such as 25 mm. (1 inch) and high collodion cotton content (3.5 per cent) in a 65 per cent dynamite, which is frequently observed, are characteristic. For this reason too short a train of explosives or too near a placement of the distance to be measured from the cap often gives incorrect results. In such a case only the initial velocity, which increases with diameter and strength of confinement and diminishes with increase of collodion cotton content, is measured.

The low initial velocity of gelatinous explosives is one of the reasons why they are not suitable for initiating explosives, such as cap charges. Small quantities detonate slowly or require a disproportionately large initial impulse to release their maximum velocity, while a blasting cap charge of a suitable explosive, such as trinitrotoluene or tetranitromethylaniline (tetryl), has the characteristic that it detonates with high velocity with a very small quantity of a priming charge of directly detonating explosive, such as mercury fulminate or lead azide.

All factors which affect the sensitiveness also affect the initial velocity.

Example 1. A 65 per cent gelatine dynamite with 3.5 per cent collodion cotton and 28 per cent potassium nitrate, detonated in a pipe 25 mm. (1 inch) in diameter 10 cm. beyond the blasting cap with a velocity of 2350 meters per second. The same explosive with 28 per cent of potassium perchlorate in place of saltpeter reached a velocity of 7000 meters per second under the same conditions. After storing for six months the initial velocity diminished in both cases, the first having a velocity of 2250, the second 2750 meters per second. After the same length of warm storage the velocities were 1500 and 1800 meters respectively. Storage thus reduced the sensitiveness, especially at elevated temperatures, but the favorable effect of the perchlorate is still felt after storage.

Example 2. A 65 per cent gelatine dynamite with 1.75 per cent collodion cotton reached a velocity of 3000 meters per second in a 25 mm. (1 inch) iron pipe 10 cm. beyond the cap. At 30 cm. beyond the cap the maximum velocity of about 7500 meters per second was found. A similar test with a gelatine containing 3.5 per cent collodion cotton gave 2200 meters 10 cm. beyond the cap and 7000 meters 50 cm. away from the cap.

Example 3. In a 40 mm. tube the same dynamite with less col-

lodion cotton reached a velocity of 6750 meters per second immediately behind the detonator, about 7500 meters 20 to 30 cm. away, while when containing a good deal of collodion cotton it reached 2400 to 2600 meters near the cap and 7500 meters 30 to 40 cm. away.

Even the lower strength dynamites show similar high velocities of detonation, for example a 40 per cent gelatine dynamite with 1 per cent collodion cotton gave about 6500 meters in a 35 mm. tube, dynamite No. 5 containing 18 to 20 per cent nitroglycerine and potassium perchlorate as the oxidizing salt 6500 to 6800 meters per second.

Products of explosion of gelatine dynamite. It is the custom to so compound all gelatine dynamites, and since a few years ago all explosives intended for mining, that the available oxygen they contain will suffice for complete combustion to carbon dioxide and water, or to have a certain excess of oxygen present which can burn the cartridge paper as well, so that no combustible or poisonous gases can occur in the gaseous products of a properly initiated explosion. Such dangerous gases are hydrogen, methane and carbon monoxide.

The new Prussian Police Order governing the sale of mining explosives, dated January 25, 1923, prescribes in sections 8 and 18 for brisant non-permissible and permissible explosives, that such explosives insofar as they may be used in underground mining, shall be compounded on a theoretical oxygen balance or an oxygen excess.

One kilogram of 65 per cent gelatine dynamite having the composition: 62.5 per cent nitroglycerine, 2.5 collodion cotton, 27 per cent sodium nitrate and 8 per cent wood meal gives the following calculated products of explosion:

	grams
CO ₂	449.03
N ₂	163.10
O ₂	44.47
H ₂ O.....	175.05
Na ₂ CO ₃	168.35
	1000.00

The explosive thus has a 4.5 per cent oxygen excess. The gaseous products of explosion, often called "fumes," have the composition given in table 36. The gases of explosion of 1 kg. of this gelatine dynamite occupy 605.7 liters calculated to 0°C. and 760 mm. pressure, or 389.6 liters after condensation of the water vapor. Their composition is as shown in table 37. The products of explosion of other

gelatine dynamites have a similar composition. When using potassium perchlorate they give a smoke of potassium chloride. The ammonium nitrate explosives leave no solid residue.

In actual gas analyses in the nickel steel bomb usually no free oxygen is found even when there is a small oxygen excess in the explosive, but rather some carbon monoxide, since some insulating material is introduced into the bomb on the wires for electrical

TABLE 36

Gaseous products of explosion of gelatine dynamite

	IN PER CENT BY WEIGHT	AFTER CONDENSATION OF THE WATER VAPOR
	per cent	per cent
CO ₂	54.00	68.4
N ₂	19.60	24.8
O ₂	5.35	6.8
H ₂ O.....	21.05	
	100.00	100.0

TABLE 37

Gases of explosion of 1 kg. gelatine dynamite

	IN PER CENT BY VOLUME	AFTER CONDENSATION OF WATER
	per cent	per cent
CO ₂	37.7	58.6
N ₂	21.5	33.4
O ₂	5.1	8.0
H ₂ O.....	35.7	
	100.0	100.0

ignition, and this consumes oxygen on combustion. Moreover the walls of the bomb and the metal parts of the blasting cap and its contents undergo a certain oxidation, so that the error in such determinations is not inappreciable, and very difficult to determine and to eliminate. Such investigations therefore have only a limited value, and we have to depend on calculation for the oxygen excess for all explosives having an oxygen excess, whose products of explosion on proper detonation are of known composition. This can be calculated

with certainty. On the other hand, with a deficiency of oxygen an explosion in the bomb also gives no correct picture of the practical conditions, since the explosive is usually fired in the bomb at very low densities of loading, while in the borehole the density of loading is 1. With incomplete combustion the density of loading has an effect upon the composition of the gases.

TABLE 38

Comparison of gelatine dynamite with blasting gelatine

	BLASTING GELATINE	65 PER CENT GELATINE DYNAMITE		
		Dynamite No. 1		Ammonia dynamite (Forsite)
		per cent	per cent	per cent
Nitroglycerine.....	92.0	62.5	62.5	63.0
Collodion cotton.....	8.0	2.5	2.5	2.0
Wood meal.....	—	8.0	8.0	5.0
Sodium nitrate.....	—	27.0	—	—
Potassium perchlorate.....	—	—	27.0	—
Ammonium nitrate...	—	—	—	30.0
Total.....	100.0	100.0	100.0	100.0
Oxygen balance.....	+0.4%	+4.4%	+3.2%	+1.5%
Density.....	1.6	1.55	1.58	1.44
Lead block expansion.....	560.0 cc.	400.0 cc.	430.0 cc.	485.0 cc.
Lead block crushing..	24.0 mm.	20.0 mm.	21.0 mm.	21.0 mm.
Maximum velocity of detonation.....	8000.0 m/s	7000.0 m/s	7000.0 m/s	7000.0 m/s
Heat of explosion, H ₂ O vapor.....	1560.0 Cal.	1235.0 Cal.	1290.0 Cal.	1300.0 Cal.
Temperature of explosion.....	3200°C.	2950°C.	3050°C.	2770°C.

Heat of explosion; temperature of explosion; strength. The 65 per cent gelatine dynamite develops a heat of explosion of 1230 to 1240 calories with water as vapor, and about 1390 Calories with water as liquid. The temperature of explosion is 2950°C. The lead block expansion of 400 cc. net, lies between guhr dynamite and blasting gelatine. This lead block expansion is approached by the strongest ammonium nitrate explosives, which give 370 to 380 cc. The

characteristic difference between the effects of the two explosives is mainly in the different densities and velocities of detonation, these with ammonium nitrate explosives generally amounting to only 1 to 1.2 and 4000 to 5000 meters per second.

TABLE 38—Continued
Comparison of gelatine dynamite with blasting gelatine

	40 PER CENT GELATINE DYNAMITE			20 PER CENT GELATINE DYNAMITE NO. 5
	Dynamite No. 3	Dynamite No. 4		
	per cent	per cent	per cent	per cent
Nitroglycerine gelatine.....	40.0	40.0	40.0	18.0-20.0
Vegetable meal.....	6.0	7.0	2.0	2.0-4.0
Trinitrotoluene.....	10.0	—	—	12.0
Dinitrotoluene.....	—	—	—	
Hydrocarbon.....	—	—	5.0	
Sodium nitrate.....	44.0	41.0	—	—
Potassium perchlorate.....	—	—	41.0	54.0
Filler.....	—	12.0	12.0	12.0
Total.....	100.0	100.0	100.0	100.0
Oxygen balance, about.....	+7.0%	+12.0%	+2.5%	+11.0%
Density, about.....	1.6	1.7	1.8	1.8
Lead block expansion, about.....	290.0 cc.	230.0 cc.	330.0 cc.	250.0 cc.
Lead block crushing, about.....	18.0 mm.	19.0 mm.	20.0 mm.	18.0 mm.
Maximum velocity of detonation, about.....	6500.0 m/s	6500.0 m/s	6500.0 m/s	6500.0 m/s
Heat of explosion, H ₂ O vapor.....	1030.0 Cal.	850.0 Cal.	1150.0 Cal.	800.0 Cal.
Temperature of explosion, about.....	2800°C.	2500°C.	3000°C.	2650°C.

Table 38 gives a review of the technical data of the most important representatives of the gelatine dynamite class in comparison to blasting gelatine.

OTHER METHODS OF MANUFACTURE OF GELATINE DYNAMITE

Of the various proposals made in the course of time to gelatinize nitroglycerine in ways other than that used by Nobel, and convert it into a plastic form and so make it the basis of plastic explosives, nothing valuable has developed aside from the previously mentioned addition of Centralite,²⁰ nor has anything of industrial importance been discovered. These processes will therefore be mentioned only briefly.²¹

According to German patent 42452, issued to the Deutsche Sprengstoff A.-G. in 1887, nitroglycerine can be gelatinized by the addition of picric acid in quantities up to 10 per cent without heating. The addition of a strong acid like picric acid would affect the chemical stability of nitroglycerine and might also set free nitric acid from the nitrates in the presence of traces of moisture always at hand.

According to German patent 108402, issued to Callenberg in 1898, the collodion cotton is first dissolved in oil of turpentine, for example, 1 part of collodion cotton in 4 parts of oil of turpentine. The mixture then gelatinizes rapidly and uniformly when warmed with nitroglycerine. Aside from the high price and the volatility of the oil of turpentine such a process is useless because collodion cotton does not dissolve to an appreciable extent in oil of turpentine, consequently the uniform distribution between nitroglycerine and collodion cotton is not appreciably facilitated, moreover uniform gelatinization without such addition offers no difficulties, and on the other hand suitable means such as aromatic nitrocompounds are available to increase the plasticity of low strength, plastic nitroglycerine explosives, and they desensitize very little.

According to German patent 172651 of 1905, issued to Schachtebeck, drying of the collodion cotton is avoided by mixing the moist collodion cotton with a corresponding quantity of powdered glue, dextrine or starch, which swell with water and withdraw the latter from the fibers of the nitrocellulose, so that gelatinization is facilitated. However, as mentioned under blasting gelatine, water does not hinder gelatinization, but merely hinders fine and uniform distribution of the collodion cotton in the nitroglycerine. This latter is not favored in the presence of swollen glue or dextrine, and moreover the water, which would otherwise be mostly evaporated, remains in the gelatine, rendering it sticky. The process therefore comes into consideration less in the case of high strength dynamites than as a means for increasing the plasticity of low strength explosives, such as the permissible nitroglycerine class.

Attempts which have been made to entirely replace the always expensive collodion cotton and convert the nitroglycerine into a gelatinized state by other agents, have just as little success. In such a case it is usually merely a question of emulsions in which the nitroglycerine is more or less firmly retained but

²⁰ Cf. Chapter on Blasting Gelatine, Increasing Gelatinizing Power.

²¹ Escapes, *Nitroglycerin und Dynamit*, Modified Gelatinizing Processes, p. 256.

which can hardly show the physical stability that the true nitroglycerine-collodion cotton-gelatines show, and which moreover have chemical disadvantages attached to them. Such substances as formaldehyde condensation products (German patent 176072) cannot for this reason displace collodion cotton because they are not cheap and must be used in far greater amounts than collodion cotton to obtain similar results (see also German patents 15073, 93351, 95390 and 110621).

German patent 180685 of 1902, issued to Bichel, according to which a colloidal solution of materials such as glue in suitable liquids of boiling points higher than water, such as glycerine, was used, attract a certain amount of attention. Glue was dissolved in glycerine by heating and stirring or by preliminary solution in water, which on further heating was evaporated from the excess of glycerine. More than five times the weight of the still warm, syrupy glue-glycerine-gelatine could be added as nitroglycerine and stirred to a stiff emulsion, which could hardly be compared to a true gelatine, but from which the liquid nitroglycerine could not escape on account of the sticky nature of the glue. An example is 63 per cent nitroglycerine, 11.5 per cent glue-glycerine in 1:7 proportions, 19.3 per cent sodium nitrate, 6.2 per cent wood meal. The "gelatine dynamite" so obtained is plastic and retains the nitroglycerine firmly, but in contrast to gelatine dynamite made with collodion cotton is greasy and sticky and does not break off the walls of the vessels easily. The strength as determined by the lead block expansion is not far below that of gelatine dynamite, 390 cc. The lack of economy of this process is explained by the large proportion of expensive glycerine required, which can be used to greater advantage as nitroglycerine, and which is replaced in the case of collodion cotton by cheaper components as oxygen consumers. The process is therefore in no way practical and suitable for the manufacture of high strength dynamites in order to save collodion cotton, and at the same time it leads to the formation of gases containing carbon monoxide, and has therefore found no application. On the other hand, the glue-gelatine has been used in the manufacture of low strength permissible explosives under the name of "Melan" in connection with a nitroglycerine-gelatine made of nitroglycerine and collodion cotton. It is emulsified with the latter, and serves for the so-called "lengthening" of the gelatine, i.e., to increase the plasticity and improve cartridgeing of low strength, gelatinous nitroglycerine explosives (see Permissible Nitroglycerine Explosives).

GELATINOUS EXPLOSIVES WITHOUT NITROGLYCERINE

The outstanding property of gelatine dynamites, namely high density and convenient, plastic, flexible form, as a result of which it can be easily pressed against the walls of the borehole and completely fill it, thus raising the effects produced, has not prevented attempts to imitate it. Attempts have been made to give all the other explosives a plastic, gelatinous form, the efforts being along the lines of replacing the always dangerous nitroglycerine.

By this is not meant the attempts of recent times to introduce other nitric esters having properties similar to nitroglycerine, such as dinitrochlorohydrine or dinitroglycol. With these esters similar results can be obtained, or even in the case of nitroglycol equal results. Since at the same time the explosives are made non-freezing they will be considered in the next chapter under "Non-Freezing Nitroglycerine Explosives."

The oldest of such efforts to produce gelatinous explosives without any nitroglycerine-gelatine led to a mixture of saltpeter or chlorate with nitrocellulose gelatinized by nitrobenzene or nitrotoluene, with the addition of some antimony sulphide, for example 21 per cent nitrobenzene, 1 per cent collodion cotton, 3 per cent antimony sulphide and 75 per cent potassium chlorate, called Kinetit.²² Such gelatinous mixtures with saltpeter cannot be detonated, and even when containing the sensitive chlorate they are sluggish and carry the detonation through the mass with difficulty, in contrast to the readily-detonating, powdery chlorate explosives. On the other hand, Kinetit was very sensitive to shock and friction, and did not last very long.

A similar explosive was produced according to British patent 22240 of 1912, by gelatinizing chlornitrobenzene, chlornitrotoluene and chlornitronaphthalene with nitrocellulose, and kneading the potassium chlorate into this. According to the United States patents 1041745 and 1040793, issued to Silberrad, gelatinous explosives are produced by the following chlorate composition: 65 to 70 per cent KClO_3 , 12 to 13 per cent nitrotoluene, 6 to 7 per cent dinitrotoluene, 6 to 7 per cent nitronaphthalene, 0.5 to 2.5 per cent soluble nitrocellulose and 5 to 6 per cent wood meal, or 63 to 70 per cent NH_4ClO_4 , 12 to 14 per cent nitrotoluene, 6 to 7 per cent dinitrotoluene, 6 to 7 per cent nitronaphthalene, 0.6 to 2.5 per cent soluble nitrocellulose and 6 per cent wood meal.

Some time earlier a gelatinous explosive consisting of 70 per cent sodium chlorate and 30 per cent collodion cotton gelatinized with the so-called liquid trinitrotoluene, a mixture liquid at ordinary temperatures or at a gentle heat, of the isomeric trinitrotoluenes obtained from the residue of the recrystallization of 2,4,6-trinitrotoluene, was proposed under the name of Gelatine-Chedditi. This was com-

²² German patent 31786 (1884), British patent 10986 (1884), French patent 163256, by Petri and Fallenstein, Düren.

pounded on an oxygen excess, in contrast to the previous gelatine chlorate explosives which all had an oxygen deficiency and consequently had given poisonous gases on explosion. This explosive came the nearest to perfection, since the nitrocompounds forming the gelatinous basis had in themselves an explosive character.

All of these gelatinous chlorate explosives had the typical sensitiveness to shock and friction of all the chlorate explosives, and in this respect were no less dangerous to handle than gelatine dynamites. On the other hand, they lacked the certain, reliable ease of detonation of dynamites, and propagated detonation with more difficulty than analogous chlorate explosives without collodion cotton and which were therefore not gelatinized and more or less pulverent, and semi-pulverent, semi-plastic, moist but non-cohesive, gelatinous masses.

The colloidal condition, which generally hinders propagation of the wave of explosion and reduces the sensitiveness, must naturally render detonation especially difficult in gelatines made from nitrocompounds which are in themselves of a weak explosive character. Even the use of the chlorates, those oxygen salts which most easily give up their available oxygen on account of their strong endothermic character and consequently raise the sensitiveness when used as explosive components, cannot offset the sluggishness of such gelatines.

The idea developed by Stettbacher in his book *Schiess- und Sprengstoffe*, Section 2, Chapter 5 on the relation between chemical constitution and explosive effect, that explosive materials with aliphatic chains, such as nitric esters like nitroglycerine and nitrocellulose, decompose relatively difficultly, and that on the other hand the tendency toward explosive decomposition of nitrocompounds having a benzene ring is considerably greater, is the result of undervaluing the striking effect of the aggregate condition, such as air trapped in powdered crystals—liquids—gelatines—cast masses, etc., and does not withstand close examination under comparable conditions.²³

The fact is that all gelatines having a relatively low true energy content and those which are not in themselves highly brisant explosives, give explosives which detonate too sluggishly. Gelatine made with a base of trinitrotoluene isomers is no exception to this, although

trinitrotoluene as a powdered crystal has a very high velocity of detonation and still a high sensitiveness.

For this reason the gelatinous explosives having a base of relatively energy-poor aromatic nitrocompounds cannot compete with gelatine dynamites.

The sensitiveness of such aromatic nitrocompound gelatines can however be raised by the addition of nitroglycerine, if low-melting or liquid eutectic mixtures of nitrocompounds at ordinary temperatures, miscible with nitroglycerine in all proportions, are gelatinized in common with the latter. In the proportion of two thirds dinitrocompound or di- and trinitrocompounds and one third nitroglycerine gelatinous explosives of a satisfactory sensitiveness to detonation can be made with the aid of chlorates as the oxidizing agents.

Since gelatines made from nitroglycerine and aromatic nitrocompounds have the non-freezing property, such explosives will for this reason be discussed in the next chapter on low-freezing and non-freezing nitroglycerine explosives.

²³ See article by the author entitled "Chemical Constitution and Explosive Effect," *Z. Schiess- u. Sprengstoffw.*, (1920), p. 5.

CHAPTER XXII

LOW-FREEZING AND NON-FREEZING NITROGLYCERINE
EXPLOSIVES

DINITROCHLOROHYDRINE AND NITROGLYCOL EXPLOSIVES

The disadvantage of nitroglycerine explosives attendant upon their relatively high freezing point and so uniformly and more or less slowly freezing in cold weather to a hard, stiff mass difficult to detonate, which only thaws slowly and therefore requires special devices in actual use, has been a problem for the chemist from the earliest time of use of nitroglycerine. Attempts have been made to reduce the freezing point of nitroglycerine so far that freezing of the explosive would be prevented at winter temperatures.

How this problem has been attacked in the course of time and how it was completely solved in a commercially satisfactory manner about two decades ago has already been described in the historical review, so that here there will be given more of the practical details of the various more or less complete solutions of this problem.

The classical work of the Swedish engineer, Sigurd Nauckhoff,¹ who first determined the molecular lowering of the freezing point of nitroglycerine by a great number of experiments, and clearly formulated the requirements which a material to be added to lower the freezing point must possess, cleared up the matter and explained the imperfection at that time of methods of producing low-freezing nitroglycerine explosives. It defined the problem and in many ways smoothed the way for its solution. However, the solution was rendered possible somewhat earlier, independent of this work, by the use of dinitroglycerine and dinitrochlorohydrine, as well as other mixed esters of glycerine and esters homologous to nitroglycerine.

It has been shown that the molecular weight of the substances dissolved in nitroglycerine to reduce the freezing point of the latter is to be sure of theoretical significance, but for actual cases plays no appreciable rôle. If E be the lowering of the freezing point, m the

concentration in per cent of the material dissolved in nitroglycerine, or g grams per 100 grams, and M its molecular weight, then

$$E = K \frac{m}{M}$$

Nauckhoff determined the constant K to be 70.5, so that the formula becomes

$$E = 70.5 \frac{m}{M}$$

Accordingly, 1 per cent of water, provided that at the temperatures in question it were soluble in nitroglycerine, would reduce the freezing point by almost 4°, 1 per cent methyl nitrate by 0.9° and 1 per cent dinitroglycerine by only about 0.4°.

Aside from the fact that these constants apply to only dilute or moderately concentrated solutions, and diminish with concentrated solutions, there is no suitable substance soluble in nitroglycerine with approximately as low a molecular weight as water, which even at relatively low concentrations would reduce the freezing point of nitroglycerine in an appreciable manner. At low temperatures water is as good as insoluble in nitroglycerine, and moreover is volatile. Methyl nitrate, which when 20 per cent of it is added must theoretically reduce the freezing point by 18°, received consideration on account of its highly brisant character and was mentioned by Nobel as a means of reducing the freezing point. Its great volatility hinders its practical use for ordinary cartridge mining explosives. Substances having a low molecular weight which have been considered are usually volatile. For this reason substances of high molecular weight were turned to, but on account of the high freezing point of nitroglycerine, which it is necessary to reduce by 20 to 30°C., it is evident that large quantities must be added, and consequently only chemical compounds very soluble in nitroglycerine can be considered, and in view of the large quantities added only compounds which have the necessary solubility and which are themselves of a pronounced explosive character can be used.

The Nauckhoff investigations and his specifications for suitable materials form the basis for the solution of the whole problem.

One other point should be mentioned. If the material which is

¹ Contribution to the Knowledge of the Freezing of Nitroglycerine and Nitroglycerine Explosives, *Z. angew. Chem.*, 1905, pp. 11 and 53.

added in considerable proportions, and which itself must have a low freezing point, also has the power of dissolving considerable nitroglycerine at low temperatures, so that the dissolved nitroglycerine in turn can reduce the freezing point of the added compound, it is peculiarly capable of fulfilling its purpose. It is evident that related nitric esters dissolved in nitroglycerine, which are miscible with nitroglycerine in all proportions, and almost all of which freeze at lower temperatures than nitroglycerine, fulfil this requirement to a great extent.

These esters, which are in themselves highly explosive compounds, are the substances which have finally solved the problem, after their power of forming with nitroglycerine the so-called eutectic mixtures having very low freezing points and small tendencies to crystallize had been recognized.

The aromatic nitrocompounds readily soluble in nitroglycerine also brought about a partial solution of the problem. The di- and tri-nitrocompounds have an explosive character and therefore do not desensitize the nitroglycerine too much.

In practice the low freezing nitroglycerine explosives are divided into two classes:

1. Nitroglycerine explosives containing aromatic nitrocompounds.
2. Nitroglycerine explosives containing related nitric esters.

To this should be added a kind of non-freezing explosives resembling dynamites:

3. Explosives having a base of dinitroglycerine, dinitrochlorohydrine or nitroglycol.

NITROGLYCERINE EXPLOSIVES CONTAINING AROMATIC NITROCOMPOUNDS

The oldest method of preventing dynamite from freezing consists in general of adding more or less nitrobenzene and nitrotoluene. Rudberg patented the addition of nitrobenzene and benzene in 1866. Nobel mentions in 1876 in his patent for gelatinized nitroglycerine among other things the addition of nitrobenzene and dinitrobenzene, and Wahlenberg and Sundström in 1877 protected the addition of *o*-nitrotoluene. From the character of the mononitrocompounds, which in themselves are not explosive, it is evident why the desired end of rendering high strength dynamites and similar strength

gelatine dynamites non-freezing was not accomplished by their aid; the assertions of the inventors were not well founded. Smaller additions failed to accomplish their purpose. The freezing point was only slightly, or not sufficiently reduced for practical purposes. With greater additions such as were practically effective the explosive was desensitized considerably and its brisance lowered too much.

The Nauckhoff tables² make this situation clear, and show that a mixture of nitroglycerine and 10 per cent nitrobenzene freezes even at +5°, with 20 per cent nitrobenzene at +2°, with 10 per cent nitrotoluene at +6° and with 22 per cent *o*-nitrotoluene at +1.5°. Thus at continued winter cold such mixtures freeze, although more slowly than pure nitroglycerine.

A dynamite containing 52 per cent nitroglycerine, 10 per cent nitrobenzene, 3 per cent collodion cotton and 35 per cent sodium nitrate would still have an oxygen balance. It would therefore produce harmless gases on explosion and be a useful explosive. It could be designated as low-freezing but not as non-freezing.

A similar explosive formerly made in Austria under the name of "Low-Freezing Dynamite I," composed of 55 per cent nitroglycerine, 10 per cent nitrotoluene, 2 per cent collodion cotton, 8 per cent wood meal, 24 per cent sodium nitrate and 1 per cent filler, was an effective explosive, but had about 16 per cent negative oxygen balance and so had the disadvantage of giving off harmful gases on explosion.

The following mixture was called "Low-Freezing Dynamite II:" gelatinized nitroglycerine 40 per cent, nitrotoluene 8 per cent, lamp-black 0.5 per cent, wood meal 4.2 per cent, rye meal 3.1 per cent, sodium nitrate 43.7 per cent and caput mortuum 0.5 per cent. This explosive, which had 20 per cent of the nitroglycerine replaced by nitrotoluene, had a better oxygen balance of only about -4 per cent.

With lower strength dynamites, nitrocompounds of this kind can give a greater degree of resistance to freezing, because with large amounts of nitrocompounds the larger quantities of oxidizing salts used give a satisfactory combustion. When required, the Carbonitfabrik in Schlebusch bei Köln furnished a so-called non-freezing gelatine dynamite composed of nitroglycerine 28 per cent, nitrotoluene 12 per cent, collodion cotton 1.5 per cent, wood meal 1 per cent, ammonium nitrate 57.5 per cent. In this case the nitroglycerine is

² *Z. angew. Chem.* (1905), p. 57.

mixed with more than 40 per cent of its weight of nitrotoluene and the total explosive oil contains 30 per cent of the latter. The explosive is gelatinous and packs well into cartridges. It has an oxygen balance of -11.4 per cent and gives a lead block expansion of 410 cc. The lead block crushing amounts to only 15 mm. as compared to 20 mm. for high strength gelatine dynamite, and its brisance is therefore lower. It also requires naturally a stronger blasting cap than dynamite made with pure nitroglycerine.

One disadvantage of this explosive is its penetrating odor of nitrotoluene and nitrobenzene, which the miners find troublesome. Its lower sensitiveness to shock and friction makes it safer to handle.

The explosive mentioned above, containing 30 per cent mononitrotoluene³ in the explosive oil mixture, freezes at $-15^{\circ}\text{C}.$ on slow cooling, and does not crystallize completely on seeding with a nitroglycerine crystal. It thaws very easily on warming slightly. At $-5^{\circ}\text{C}.$ it is quite soft. It is therefore designated as practically non-freezing for German winter climate.

In order to desensitize the nitroglycerine less and reduce the brisance of the dynamite less by the added compounds the di- and trinitroderivatives, especially of toluene, have been proposed instead of the mononitrocompounds, to reduce the freezing point.⁴ Theoretically these, as compared to the mononitrocompounds, will reduce the freezing point less on account of their higher molecular weight, according to Nauckhoff with 20 per cent nitrobenzene by $11.4^{\circ}\text{C}.$, with 20 per cent dinitrobenzene $8.4^{\circ}\text{C}.$, which is not of very much practical importance. The practical difficulty in obtaining a complete effect lies here in the lower solubility of the high-melting di- and trinitrotoluene in nitroglycerine at low temperatures, while on the other hand large proportions are necessary to render the mixtures in question non-freezing at winter temperatures. Nauckhoff calculated for a gelatinized solution of 100 parts of nitroglycerine and 20 parts of nitrobenzene a freezing point of $-1.4^{\circ}\text{C}.$ and determined experimentally $+2.0^{\circ}\text{C}.$, for 20 parts dinitrobenzene he calculated $+1.2^{\circ}$ and found $+4.0^{\circ}$. With the nitrotoluenes the relations were similar.

³ Mononitrotoluene has been found to be very poisonous on contact with the skin.—TRANSLATOR.

⁴ French patent 333502 (1903), British patent 14827 (1903), and 25797 (1904) of the Soc. anonyme des poudres et dynamites, Paris.

According to tests made by the author 100 parts nitroglycerine at $20^{\circ}\text{C}.$ hold in solution 35 parts of 2,4-dinitrotoluene and 30 parts of 2,4,6-trinitrotoluene, while at their melting points these nitrocompounds mix with nitroglycerine in all proportions. At low temperatures of $0^{\circ}\text{C}.$ and below the solubility coefficient falls considerably. The conditions in the case of the eutectic mixtures of the various isomers of these nitrocompounds frequently used in actual practice, are somewhat more favorable. At ordinary temperatures they are somewhat oily and are known under the names of bi-drop oil, metabi-nitrotoluene and liquid trinitrotoluene. Addition of such liquid isomers of nitro-derivatives of toluene is the object of British patent 25797 (1904).

Leroux⁵ proposed the addition of solid di- and trinitrotoluene. The statement that 10 per cent of these was capable of lowering the freezing point of nitroglycerine to $-25^{\circ}\text{C}.$ is naturally incorrect.

The practical behavior of mixtures of nitroglycerine and aromatic nitrocompounds, as well as the explosives made therefrom, can be determined experimentally by exposing them for a long time to low temperatures, for example in a refrigerating machine, and seeding them with a crystal of nitroglycerine. Often on account of the stubborn supercooling phenomenon and the relatively slow tendency toward crystallization of such mixtures, an explosive which remains liquid or soft on simple cooling without crystallization gives no certain conclusion as to the behavior on long transportation or long storage at winter temperatures. Solutions of 10 to 30 per cent di- or trinitrotoluene in nitroglycerine freeze completely at $-15^{\circ}\text{C}.$, and remain frozen at $0^{\circ}\text{C}.$, solutions of 10 per cent mononitrobenzene or mononitrotoluene freeze almost completely, of 20 per cent for the greater part, and 30 per cent partly. At $0^{\circ}\text{C}.$ the 10 per cent solution does not alter, the 20 per cent solution thawed appreciably and formed a thin paste of crystals, and the 30 per cent thawed almost completely, corresponding to the Nauckhoff determinations.

Also gelatines containing 15 to 30 per cent di- or trinitrotoluene freeze completely at $-15^{\circ}\text{C}.$ and remain solid at $0^{\circ}\text{C}.$ Gelatines containing 15 per cent of the mono-derivative freeze at $-15^{\circ}\text{C}.$ and become soft at $0^{\circ}\text{C}.$, while with 30 per cent the gelatines become stiff after a long time at $-10^{\circ}\text{C}.$ but not hard, and soften again at $-5^{\circ}\text{C}.$

⁵ International Congress, Rome, 1906, Report II, p. 576.

These observations give an outline of the degree of resistance to freezing obtainable with dynamites containing such added compounds.

Herlin has derived a formula for the calculation of eutectic mixtures of nitroglycerine with any nitrohydrocarbon,⁶ but on the whole experiments with most of the nitrocompound mixtures used, which often do not crystallize uniformly and have no sharp crystallizing point, should lead to satisfactory conclusions.

According to Herlin's eutectic diagram the lowest crystallizing point of a nitroglycerine-nitrobenzene mixture is -14°C . for the proportion 45 per cent nitrobenzene and 55 per cent nitroglycerine, for *o*-nitrotoluene at -22°C . at a 50:50 proportion, and for the so-called liquid dinitrotoluene at -20°C . at a 40 per cent nitroglycerine: 60 per cent dinitrotoluene ratio. According to this diagram a mixture of 60 per cent nitroglycerine and 40 per cent dinitrotoluene freezes at -9°C .

When it is considered that dinitrotoluene itself is capable of explosive decomposition and consequently does not desensitize the nitroglycerine too severely, it is evident that with such a mixture a dynamite which will not freeze at moderate winter temperatures can be produced, according to the following approximate formula:

	per cent
Nitroglycerine.....	39
Liquid dinitrotoluene.....	24
Collodion cotton.....	2
Wood meal.....	5
Sodium nitrate.....	30
	<hr/> 100

As compared to gelatine dynamite made with pure nitroglycerine such an explosive naturally has the disadvantage of an unfavorable oxygen balance (about -19 per cent) and consequently forms gases rich in carbon monoxide when detonated.

Naturally this non-freezing dynamite is also considerably less brisant than 65 per cent gelatine dynamite. The combustion formula can be improved by reduction in the gelatine content and increase in the sodium nitrate. The strength of the pure, high-freezing, high-strength dynamites naturally cannot be obtained in this way. A

⁶ British patent 26493 (1913); *Z. Schiess- u. Sprengstoffw.*, p. 345 (1919).

dynamite with only about 24 per cent dinitrotoluene (of the nitroglycerine) and of the following formula:

	per cent
Nitroglycerine.....	48
Liquid dinitrotoluene.....	15
Collodion cotton.....	2
Wood meal.....	5
Sodium nitrate.....	30
	<hr/> 100

has a better combustion equation, with an oxygen deficiency of only 8 per cent. It gives a 350 cc. lead block expansion, 17.5 mm. crushing, detonates with a No. 1 cap and propagates detonation in the open in 25 mm. cartridges to a distance of 6 cm. Therefore the nitroglycerine is only slightly desensitized by a 24 per cent dinitrotoluene content. According to the Herlin diagram this explosive would freeze at about -1°C ., which just about agrees with Nauckhoff, and it can therefore be regarded as a low-freezing explosive, although it naturally will not withstand long periods of cold weather.

According to Stettbacher⁷ explosives similar but containing nitrate of ammonia and a mixture of equal parts of nitroglycerine and dinitrotoluene were used in Switzerland with good results under the name of "Gelatine-Telsit" and "Gamsit" in the construction of the great Alpine tunnels. They are made by the Fabrik Isleten am Vierwaldstätter See and Gamsen bei Brig respectively. According to the Herlin diagram such mixtures would freeze at only about -14°C .

A Gelatine-Telsit of the following composition:

	per cent
Nitroglycerine.....	22.0
Dinitrotoluene.....	21.0
Collodion cotton.....	1.5
Ammonium nitrate.....	55.5
	<hr/> 100.0

on testing gave the following results:

Oxygen balance.....	-12.6%
Lead block expansion.....	380.0 cc.
Lead block crushing.....	14.6 mm.
Ease of detonation.....	No. 6 Cap
Velocity of detonation.....	6700.0 m/s
Density.....	1.46

⁷ Stettbacher, *Schiess- und Sprengstoffe*, p. 139, also Swiss patent 48097 (1909).

Thus the desensitization of the nitroglycerine required a strong initial impulse, but such an explosive when strongly confined gives a good brisance. On the other hand the products of explosion naturally contained carbon monoxide in no inconsiderable quantities.

During the World War the so-called liquid trinitrotoluene was used in place of dinitrotoluene, the sensitiveness to detonation and brisance being improved thereby.

Vergé⁸ describes similar explosives containing liquid nitrocompound mixtures of low freezing point. They are obtained by nitrating to the di-stage a mixture of isomeric nitrotoluenes rich in *m*-nitrotoluene and dissolving 20 to 25 per cent trinitrotoluene in the oily products obtained. In this way a mixture of nitro derivatives of toluene can be obtained which crystallizes only below 0° and is particularly well suited for the manufacture of non-freezing dynamite.

Vergé gives the following examples:

1. Nitroglycerine.....	40.0	Gelatine, 62.0 per cent
Liquid nitrocompounds.....	17.0	
Gun cotton.....	5.0	
Ammonium perchlorate.....	38.0	
	100.0	
Oxygen balance.....	-5.4	
2. Nitroglycerine.....	37.0	Gelatine, 56.5 per cent
Liquid nitrocompounds.....	15.0	
Gun cotton.....	4.5	
Ammonium perchlorate.....	25.2	
Sodium nitrate.....	18.3	
	100.0	
Oxygen balance.....	+1.1	

In this case about 40 per cent of its weight as nitrocompound mixtures has been added to the nitroglycerine, and the explosive oil mixture contains about 30 per cent of aromatic nitrocompounds. This practical, low-freezing explosive mixture should show a very good sensitiveness and strength, particularly with ammonium perchlorate present. The latter is made in France and Sweden, but has not been used in Germany up to the present time on account of its high price.

⁸ Swiss patents 66131 (1913) and 66511, and Patents of addition 67356, 67359 and 67709 (1913). Also *Z. Schiess und Sprengstoffw.* (1915), pp. 104 and 158.

When ammonium perchlorate is present in an explosive, use underground requires a corresponding addition of sodium nitrate to combine with the hydrochloric acid set free on explosion and fix it as sodium chloride.

Two additional explosive mixtures according to the Vergé patents are shown in table 39. From this table it is evident that replacement of the sodium nitrate by a more sensitive oxidizing salt

TABLE 39
Two explosive mixtures according to the Vergé patents

	I	II
	per cent	per cent
Nitroglycerine.....	38	41
Liquid nitrocompounds*.....	16	18
Collodion cotton.....	2	3
Sodium nitrate.....	18	—
Ammonium perchlorate.....	26	—
Potassium perchlorate.....	—	38
	100	100
Oxygen balance.....	+1.0%	-1.1%
Lead block expansion.....	450.0 cc.	405.0 cc.
Lead block crushing.....	20.6 mm.	18.2 mm.
Sensitiveness.....	Cap No. 1	Cap No. 1
Propagation, 25 mm. cartridges in the open air.....	4.0 cm.	4.0 cm.
Velocity of detonation in 35 mm. diameter...	6600.0 m/s	7300.0 m/s
Density.....	1.52	1.57

* Solution of 20 parts trinitrotoluene in 80 parts liquid metadinitrotoluene.

according to this patent allows gelatine dynamites to be made which are very little inferior from the practical point of view to the 65 per cent dynamite, in spite of a lower nitroglycerine content. At moderate winter temperatures they are at least low-freezing.

Low-freezing blasting gelatine

According to Stettbacher⁹ a so-called special blasting gelatine has been furnished to a large extent in Switzerland, for example in the construction of the Jungfrau tunnel, by the Dynamitfabrik Isleten,

⁹ Stettbacher, *Schiess- und Sprengstoffe*, p. 135.

in which a certain amount of the nitroglycerine has been replaced by aromatic nitrocompounds. It forms a yellow-red, rubbery mass having a specific gravity of 1.58 and has an expansion of the lead block only slightly lower than that of ordinary blasting gelatine. It is less sensitive to shock than the latter and only detonates at twice as high a drop of the falling weight. It is said to withstand long continued cooling to several degrees below 0°C. without freezing. On the other hand it has the disadvantage of forming gases on explosion which contain carbon monoxide.

NITROGLYCERINE EXPLOSIVES CONTAINING RELATED NITRIC ESTERS

A severe explosion of frozen dynamite at the Gneisenau Mine in 1902 caused a renewal of attempts to make non-freezing dynamites. In 1903 patents were taken out by Mikolajzak for the manufacture and use of glycerine dinitrate, and from this time on the explosive industry turned industriously to the study of the lower glycerine nitrates and mixed nitric esters of glycerine as well as other nitric esters related to nitroglycerine, and investigated them as to their capability of forming non-freezing explosive oil mixtures with nitroglycerine, suitable for the manufacture of non-freezing dynamites.

The aromatic nitrocompounds used up to this time for the same purpose differed from these nitric esters in that the latter had an appreciably higher strength. The most important, dinitroglycerine, dinitrochlorohydrine, tetranitrodiglycerine and nitroglycol either stood only slightly below nitroglycerine or equalled it in this respect. Furthermore they remained liquid even at low temperatures and mixed with nitroglycerine in all proportions even at low temperatures, whereas the higher nitrated nitrocompounds were relatively slightly soluble in nitroglycerine at such temperatures. Also their relatively favorable combustion equation or oxygen balance made it possible, even when using the large additions of them to nitroglycerine necessary to obtain absolute non-freezing properties, to produce high strength dynamites containing large quantities of explosive oils having a complete combustion equation, which consequently gave gases on explosion which were free from carbon monoxide.

Dinitroglycerine

Since dinitroglycerine contains about 85 per cent of the energy of nitroglycerine it can readily be deduced that mixtures of the two differ only slightly in explosive strength from nitroglycerine. In addition to this there is the fact that nitroglycerine contains a slight oxygen excess (3.5 per cent), which to a certain extent can equalize the oxygen deficiency of the dinitroglycerine (17.6 per cent), so that a mixture of 83 per cent nitroglycerine and 17 per cent dinitroglycerine gives complete combustion and therefore theoretically the highest explosive strength.

However, such a mixture freezes at winter temperatures. On the other hand, explosives whose oil consists of 60 to 70 per cent nitroglycerine and 40 to 30 per cent dinitroglycerine freeze with difficulty and thaw again very easily at mild temperatures, and mixtures of equal parts are practically incapable of freezing, insofar as observations in German winter climates are concerned.

A guhr dynamite containing a mixture of equal parts of di- and trinitrate gives a lead block expansion of 295 cc. as compared with 325 cc. with pure nitroglycerine, or about 90 per cent of the latter.

With the corresponding 65 per cent gelatine dynamite these values are 350 cc. and 390 cc., so that the proportion is therefore the same. Such a dynamite composed of 31.5 per cent trinitrate, 31.5 per cent dinitrate, 2 per cent collodion cotton, 29 per cent sodium nitrate, 6 per cent wood meal still had an oxygen excess of 1.3 per cent and therefore gave no carbon monoxide on explosion.¹⁰

Mikolajzak gives among other the following examples of non-freezing dynamites:

<i>a. Guhr dynamite</i>	
	<i>per cent</i>
Dinitrate (60 per cent).....	45.0
Trinitrate (40 per cent).....	30.0
Guhr.....	23.0
Chalk.....	2.0
<i>b. Blasting gelatine</i>	
	<i>per cent</i>
Trinitrate (about 85 per cent).....	78.0
Dinitrate (about 15 per cent).....	14.0
Collodion cotton.....	8.0

¹⁰ This might not be true if a paraffined paper shell were used.—TRANSLATOR.

Blasting gelatine freezes more slowly than guhr dynamite and gelatine dynamite, yet the above mixture is likely to freeze.

c. Gelatine dynamite

	per cent
Dinitrate (60 per cent).....	38.4
Trinitrate (40 per cent).....	25.6
Collodion cotton.....	1.7
Sodium nitrate.....	27.0
Wood meal.....	7.3

d. Ammonia gelatine dynamite

	per cent
Dinitrate.....	40.0
Collodion cotton.....	1.2
Turmeric meal.....	4.8
Ammonium nitrate.....	54.0

TABLE 40
Composition of "Tremonte"

	GELATINE-TREMONT	
	I	II
	per cent	per cent
Gelatinized di-trinitrolycerine mixture.....	47.5	30.0
Dinitrotoluene.....	5.0	10.0
Wood meal.....	5.0	2.0
Ammonium nitrate.....	22.5	40.0
Sodium nitrate.....	20.0	18.0
Lead block expansion.....	400 cc.	375 cc.

This explosive had only a slight oxygen deficiency, 2.4 per cent, and a very good strength in the lead block test, 400 cc. net. Such an explosive was furnished for a long time by the Castrop-Sicherheits-sprengstoff A.-G. from their Rummenohl Plant at Hagen in Westfalia under the name of "Tremonte." (See table 40.) This explosive was compounded on about an even oxygen balance and therefore gave harmless gases on explosion.

The same company produced permissible explosives having a dinitrolycerine basis, which were non-freezing, which will be taken up in the next chapter.

Dinitrolycerine was gradually displaced by dinitrochlorohydrine, which in addition to greater convenience in handling had the advan-

tage over the former in being insoluble in water and safer to handle, while dinitrolycerine had a higher sensitiveness to mechanical effects and did not differ in this respect much from nitrolycerine.

On the other hand, the doubts expressed by Will¹¹ did not prove to be well founded. Will feared that dinitrolycerine, on account of its ability to form an hydrate melting only at +26°C., and its hygroscopicity in the form of this hydrate, would freeze in the explosives and not be suitable for the manufacture of non-freezing dynamites.

In actual practice the explosives in question did not appear to ever freeze, even when moist dinitrolycerine was used. In this connection it should be noted that the Mikolajzak method of manufacture used by the Castrop Company formed both isomers of dinitrolycerine in about the proportions of 60 parts of the form, producing hydrated crystals to 40 parts of the non-crystalline form, and that the tendency to crystallize of the commercial product was apparently very slight.

Dinitrochlorohydrine

The addition of dinitrochlorohydrine to nitrolycerine explosives to render the latter non-freezing was patented¹² in 1904 by the Dynamit A.-G. vorm Nobel & Co., which soon afterward built at the Schlebusch (near Cologne) Dynamite Plant an extensive factory for the manufacture of monochlorohydrine from glycerine and sulphur chloride, nitrating the monochlorohydrine to dinitrochlorohydrine in their dynamite plant, and putting out non-freezing dynamites containing a corresponding nitrolycerine content. F. Roewer describes this in detail.¹³

Like dinitrolycerine, dinitrochlorohydrine is able to reduce to a great extent the freezing point of nitrolycerine. If mixtures of 20 to 30 per cent of dinitrochlorohydrine and 80 to 70 per cent nitrolycerine are cooled to temperatures of 15 to 18°C. below 0°C. and seeded with a crystal of nitrolycerine, after several days the nitrolycerine finally crystallizes out of the mixture, while the dinitrochlorohydrine remains liquid throughout the mass. On the other hand, cartridges containing 20 per cent dinitrochlorohydrine in nitrolycerine, when frozen in this way, thawed at 0°C. When 25

¹¹ Reported at other points under Dinitrolycerine.

¹² German patent 183400.

¹³ Z. Schiess- u. Sprengstoffw. (1906), p. 228.

per cent dinitrochlorohydrine was used the cartridges were still soft at -3°C . Moreover, the supercooling phenomenon or crystallizing tendency of nitroglycerine is appreciably affected by such additions, so that without seeding by frozen nitroglycerine such cartridges do not freeze on continued exposure to cold weather, in contrast to those containing pure nitroglycerine. If the proportion of dinitrochlorohydrine amounts to 30 per cent of the explosive oil even seeded cartridges freeze only partially in cold weather, and do not become hard throughout.

A mixture of 60 per cent nitroglycerine and 40 per cent dinitrochlorohydrine can be stored for a week at -15°C . without freezing, only the seeding crystal growing somewhat in size. Even on immersion for several hours in ether cooled by solid carbonic acid to -50° to -60°C . crystallization did not take place. The liquid became more viscous, and at -15°C . it became liquid again. If the propor-

TABLE 41
Lead block expansion of non-freezing dynamites

	GUTH DYNAMITE	BLANTING GELATINE	GELIGNITE
	cc.	cc.	cc.
a. With pure nitroglycerine.....	300	555	395
b. With 20 per cent dinitrochlorohydrine	301	541	384

tion of dinitrochlorohydrine were still further raised the seeding crystal itself dissolved at -10°C . According to this, 40 parts of dinitrochlorohydrine can keep 60 parts of nitroglycerine in solution at -15°C .

In actual practice it has been found that dynamite in which 20 to 25 per cent of the nitroglycerine has been replaced by dinitrochlorohydrine, may be regarded as low-freezing, and that at a 30 per cent addition it can be called non-freezing for European winter climates.

Since dinitrochlorohydrine itself is a highly brisant explosive with 70 per cent of the energy content of nitroglycerine, it is evident that such additions can only inappreciably reduce the effectiveness of the explosives in question. Roewer¹⁴ in table 41 gives the data on the strength of non-freezing dynamites with a 20 per cent addition.

¹⁴ *Loc. cit.*

He calculates the thermochemical data and gas development as shown in table 42. Even with a 30 per cent dinitrochlorohydrine addition the explosive strength is not injured appreciably.

TABLE 42
Thermochemical data and gas development of non-freezing dynamites

	HEAT OF EXPLOSION PER KILOGRAM	TEMPERATURE OF EXPLOSION	QUANTITY OF GAS PER KILOGRAM
	calories	$^{\circ}\text{C}$.	liters
a. Gelatine dynamite: 63 per cent nitroglycerine 2 per cent collodion cotton 26 per cent sodium nitrate 9 per cent wood meal	1244	2939	716.8
b. Low-freezing gelatine dynamite: 50.4 per cent nitroglycerine 12.6 per cent dinitrochlorohydrine 2.0 per cent collodion cotton 26.0 per cent sodium nitrate 9.0 per cent wood meal	1278	2835	687.2

TABLE 43
Comparison of non-freezing dynamite with pure (nitroglycerine) dynamite

	LEAD BLOCK EXPANSION	CRUSHING EFFECT
	cc.	mm.
a. Gelatine dynamite: 63 per cent nitroglycerine 2 per cent collodion cotton 28 per cent sodium nitrate 7 per cent wood meal	415	21
b. Non-freezing gelatine dynamite: 44 per cent nitroglycerine 19 per cent dinitrochlorohydrine 2 per cent collodion cotton 28 per cent sodium nitrate 7 per cent wood meal	398	19

The author found the values with non-freezing dynamite as compared with pure (nitroglycerine) dynamite to be as shown in table 43.

The expansion of the non-freezing explosives is thus 96 per cent, the crushing effect 90.5 per cent, of that of ordinary dynamite. The oxygen balance of the non-freezing dynamite is +1.8. It therefore develops no carbon monoxide on detonation.

The hydrochloric acid set free on explosive decomposition of dinitrochlorohydrine, which could injure miners in underground operations, is neutralized by the carbonate formed from the saltpeter, and converted into chloride. It should be noted here that explosives containing dinitrochlorohydrine for underground use should always contain a quantity of alkali nitrate equivalent to the chlorine present. This is usually the case with ordinary dynamite.

Practical use and tests in the bomb have shown that dinitrochlorohydrine explosives containing a corresponding content of alkali nitrate actually give gases of explosion free from hydrochloric acid.

Gelatinous explosives containing mainly dinitrochlorohydrine, with only a small amount of nitroglycerine, have been popular for a long time. They are both non-freezing and safe to handle.

Dinitrochlorohydrine has also been used for the manufacture of non-freezing, safety and permissible explosives. They will be considered in chapter XXIII.

Tetranitrodiglycerine or nitropolyglycerine

Nitrated polymerized products of glycerine were proposed even earlier than the above-described nitric esters for the manufacture of low-freezing dynamites, as a matter of fact by Wohl in 1890.¹⁶ However, his process of heating glycerine, perhaps mixed with methyl, ethyl and other alcohols and with addition of concentrated sulphuric acid to 130 to 140°C., forming in addition to di- and triglycerine glycerine esters or their polymers, had considerable commercial disadvantages which stood in the way of practical introduction. Distillation of the raw material would have raised the cost of the raw material for nitration considerably, and the former contained resinous materials caused by the action of the sulphuric acid, which rendered separation and stabilization of the products of the nitration difficult on account of emulsion formation.

It was known even earlier that the various kinds of commercial glycerine gave nitroglycerines which differed as regards ease of

¹⁶ German patent 58957.

crystallization. The work on the question of reducing the freezing point of nitroglycerine by the addition of related nitric esters caused the suspicion that the greater or lesser content of diglycerine in dynamite glycerine, which diglycerine on nitration was converted into the viscous, non-freezing tetranitrodiglycerine, was the reason for the different behavior.¹⁶ Will followed this up and prepared mixtures of glycerine and diglycerine suitable for nitration, which gave non-freezing explosive oils having a corresponding tetranitrodiglycerine content.¹⁷ The latter differed as little from nitroglycerin in strength and brisance as the corresponding mixtures with dinitroglycerine and dinitrochlorohydrine (see Diglycerine and Tetranitrodiglycerine). Since tetranitrodiglycerine had just about as favorable decomposition equation as dinitroglycerine the same thing applies

TABLE 44
Examples of non-freezing straight dynamite

	I	II
	per cent	per cent
Nitroglycerine.....	25	15
Tetranitrodiglycerine.....	15	15
Wood meal.....	10	10
Sulphur.....	—	3
Rosin.....	—	2
Sodium nitrate.....	50	55

to the products of explosion of non-freezing explosives made from it as for dynamites containing dinitroglycerine. Explosives containing 20 to 25 per cent of tetranitrodiglycerine are non-freezing at ordinary winter temperatures.

In Germany the process has up to the present time not been used in actual practice because the manufacture of dinitrochlorohydrine, which served the same purpose, was more convenient on a commercial scale.

United States patent 855595, issued to the duPont de Nemours Powder Company, refers to the same process of partial condensation

¹⁶ Kast, *Spreng- und Zündstoffe*, p. 152; *Z. Schiess- u. Sprengstoffw.*, I, p. 231-232 (1906).

¹⁷ Will, same.

of glycerine and nitration of the product obtained.¹⁸ Patent 852142 gives the examples of non-freezing straight dynamites¹⁹ shown in table 44.

Mixed glycerine esters: Acetyldinitrolycerine (dinitroacetin) and Formyldinitrolycerine (dinitroformin)

These products have been proposed by the Italian Vezio Vender for the manufacture of non-freezing explosive oil mixtures.²⁰ According to him the addition of 10 to 30 per cent to nitroglycerine is sufficient to produce dynamites which only freeze at -20°C ., even when seeded with a crystal of nitroglycerine. According to tests by the author cartridges of dynamite in which 20 per cent of the nitroglycerine had been replaced by acetyldinitrolycerine, froze at winter temperatures. Mixtures of 70 per cent nitroglycerine and 30 per cent of the acetyl ester freeze only partially at -20°C ., when seeded with a nitroglycerine crystal, and do not solidify completely. They thaw again below 0°C . Thus acetyldinitrolycerine is as good as dinitrochlorohydrine, but since the former is a weaker explosive and has a less favorable decomposition equation the dinitrochlorohydrine has assumed first place.

Dinitroformin is just as effective as regards prevention of freezing, but on account of the expensive manufacture of the formin from glycerine and oxalic acid it appears to have found no commercial use. Its brisance is naturally superior to that of dinitroacetin.

¹⁸ See also British patent 264800 of 1926 and 265146 of 1926 to Henkel & Cie. for manufacture of polyglycerine.

¹⁹ Rosin has not been used in the United States for a great many years. For many years low-freezing explosives in the United States have contained from 22 to 35 per cent tetranitrodiglycerine, often with the addition of di- and trinitrotoluene also. Dinitrochlorohydrine has been used to only a very limited extent, mainly by the former Aetna Company. It can almost be said to have not been a factor in low-freezing explosives. At the present time all blasting explosives in the United States, except blasting gelatine which is hardly used at all, are furnished in the low-freezing form unless that containing nitroglycerine alone is specially ordered for special purposes. This applies both summer and winter, since explosives may be stored a long time.

—TRANSLATOR.

²⁰ *Z. Schiess- und Sprengstoffw.*, II, pp. 21 and 195 (1907), also Part II of this book.

Butylene glycol dinitrate

According to United States patents 994841 and 994842 (1911) 1,3-butylene glycol dinitrate in admixture with nitroglycerine is used as the basis of non-freezing explosives. Its effectiveness in this respect should not be doubted, but the rather inconvenient manufacture of the butylene glycol from acetaldehyde via aldol by reduction of the latter,²¹ and the difficult nitration of the glycol²² have stood in the way of commercial application. As regards explosive strength it is inferior to the other nitric esters used for the same purpose.

Nitroglycol and methylglycol dinitrate (α -propylene glycol dinitrate)

These two esters have been proposed as additions to nitroglycerine, to prevent freezing of the latter, in German patent 179789 of 1904. While propylene glycol dinitrate has not up to the present received commercial consideration, on account of the difficulty in obtaining the propylene glycol and some difficulty in nitration,²³ nitroglycol combines all the properties required for the purpose (see Part II). It is somewhat superior to nitroglycerine in brisance, it decomposes into carbon dioxide, water and nitrogen, and has an excellent gelatinizing power, so that gelatine dynamites containing a partial replacement of nitroglycerine by nitroglycol differ not in the slightest in explosive strength from ordinary gelatine dynamites, and in addition have the great advantage of not freezing. The somewhat higher volatility of the nitroglycol is a certain defect, which during manufacture can give rise to physiological disturbances as with nitroglycerine but to a greater degree.

At the time of the introduction of this category of non-freezing dynamites containing nitric esters no economical synthesis of the glycol was known. When the scarcity of glycerine during the war

²¹ United States patent 1008333.

²² See Part II, Butylene Glycol Dinitrate.

²³ United States patents 1307032; 1307033; 1307034; 1371215 show a method of manufacture of a mixed ethylene propylene glycol from "cracked" oil gases, satisfactory methods of nitration and stabilization, and explosives made with suitable proportions of these mixed esters, which practical tests in actual use showed could not be frozen even at temperatures prevailing in winter along the Canadian border, or -10 to -30°F .—TRANSLATOR.

turned attention to glycol syntheses and caused them to be developed, many gelatine dynamites containing mixtures of nitroglycerine and nitroglycol were supplied, and they had the advantage of not freezing.²⁴

²⁴ Ethylene glycol has been manufactured commercially for almost two years by the Carbide & Carbon Chemicals Corporation, a part of the Union Carbide and Carbon Corporation, N. Y. The production at South Charleston, West Virginia, was more than 5,000,000 pounds in 1926, and there is every indication that the total output in 1927 will be much greater. It is evident that the manufacture of ethylene glycol has already taken a definite place in American chemical industry.

The researches conducted at the Mellon Institute, Pittsburgh, supplemented by extensive practical experience, make it clear that ethylene glycol is not a mere substitute for glycerine, but is actually superior to glycerine in many respects.

It will interest European explosives specialists to learn that every large manufacturer of explosives in the United States is now using ethylene glycol in dynamite. Ethylene glycol can be readily nitrated, and its inclusion in dynamite gives a non-freezing product without diminution of sensitiveness to detonation, which is not the case with polymerized glycerine, used hitherto for the same purpose. For further information refer to Rinkenbach, Bureau of Mines, *Chemical and Metallurgical Engineering*.

Because of the nature of the process of manufacture of ethylene glycol its price does not follow that of glycerine. The price has been set by the manufacturer at 30 cents per pound (2.80 Mark per kg.) in spot quantities. This price has not varied during the whole of last year, whereas the cost of chemically pure glycerine has ranged from 25 to 30 cents per pound. It is understood that large consumers of ethylene glycol on a contract basis have obtained prices considerably lower than 30 cents per pound.

The American producer has no intention of competing directly with glycerine manufacturers, taking the view that both products have their specific uses. In addition to ethylene glycol the above company is directing its activities toward production of other compounds such as ethylene glycol mono-ethyl ether (cellosolve), which has already reached an important position in lacquers. (*The Chemical Age*, London, May 7, 1927, p. 442; also *Chem. and Met. Eng.*, April, 1927, p. 213.)

In Germany ethylene glycol is now manufactured in large quantities by the I. G. Farbenindustrie A.-G. at Ludwigshafen. For a year or so explosives manufacturers have used nitroglycol mixed with nitroglycerine to make non-freezing gelatine dynamites. It seems to be a matter of a short time only before nitroglycol will supplant entirely the dinitrochlorohydrine, even in Germany, for all kinds of uses in explosives, on account of its lower price.

—Recent note by the author.

DINITROCHLOROHYDRINE AND NITROGLYCOL EXPLOSIVES

Among the non-freezing explosives similar to dynamite, used occasionally and still made, are gelatinous mixtures formed of pure nitroglycol and dinitrochlorohydrine, the latter containing quantities of nitroglycerine. With these nitric esters explosives can be made which differ considerably from dynamite in having a very low sensitiveness to mechanical influences and safety on heating and burning, and because of this a greater degree of safety during transportation, so that they belong to another group. For this reason such explosives are permitted on German Railroads as unrestricted freight.²⁵

Dinitrochlorohydrine explosives

The dinitrochlorohydrine used for these explosives is usually made from commercial monochlorohydrine obtained by direct chlorination of glycerine, containing unchanged glycerine, and therefore being a mixture consisting mainly of dinitrochlorohydrine with a little nitroglycerine, usually 15 to 20 per cent of the latter. At this degree of dilution the characteristic properties of nitroglycerine, such as high sensitiveness to shock, are masked and do no harm to the safety in handling of the explosives in question. The railway regulations permit a total of 5 per cent nitroglycerine in such explosives. The most important representatives are:

Gelatine-Astralit. The plastic nature of this mixture is increased by a certain content of aromatic nitrocompounds such as dinitrotoluene and trinitrotoluene. Ammonium nitrate is preferred as the oxidizing salt, together with sufficient alkali nitrate to combine with the hydrochloric acid set free from the dinitrochlorohydrine on explosion.

According to the definition of the railway regulations, Gelatine-Astralit, for example, should have the following composition:

	maximum
Dinitrochlorohydrine.....	50
Nitroglycerine.....	5
Collodion cotton.....	2

aromatic nitrocompounds containing a maximum of 4 per cent trinitrotoluene, vegetable meal, ammonium nitrate, potassium or sodium nitrate or a mixture of both, also hydrocarbons.

²⁵ See Appendix C of the Railway Regulations, I, IaA, Explosives, Group c, Ammonium Nitrate Explosives.

Gelatine-Astralit I, II, etc., should have the following composition:

Dinitrochlorohydrine.....	maximum 20
Nitroglycerine.....	5
Collodion cotton.....	1

di- or trinitrotoluene, or other organic nitrocompound which is not more dangerous than trinitrotoluene, of such trinitrocompounds a maximum of 15 per cent ammonium nitrate, sodium nitrate and vegetable meal.

According to the first list of mining explosives in the new Prussian police regulations, which came into effect January 23, 1923, embracing

TABLE 45
Comparison of 85 per cent dynamite with Gelatine-Astralit

	GELATINE- DYNAMITE	GELATINE- ASTRALIT
Gaseous products of explosion per kilogram at 0°C., and 760 mm.....	605.7 liters	771.0 liters
Heat of explosion.....	1234.0 Cal.	1127.5 Cal.
Temperature of explosion.....	2950.0°C.	2534.0°C.
Specific pressure calculated therefrom.....	7162.0 atm.	7927.0 atm.
Density.....	1.55	1.45
Maximum velocity of detonation.....	7500.0 m/s	7300.0 m/s
Brisance value (product of specific pressure,* density and velocity of determination.....)	832,575	839,013
Lead block expansion.....	400.0 cc.	400.0 cc.

* Specific pressure: $P = V_{at} (273 + t) / 273$, where V_{at} = volume of the gaseous products of explosion produced at 0°C. and 760 mm., from 1 kg. of the explosive, and t = temperature of explosion.

all explosives permitted for use in Prussian mining, in place of the above explosives in the operations in question the so-called ammonia gelatine will be used, which should have the following composition:

Dinitrochlorohydrine, of which up to 5 per cent of the total explosive may be replaced by nitroglycerine.....	per cent 28-33
Collodion cotton.....	1-3
Ammonium nitrate.....	45-50
Alkali nitrate.....	10-15
Nitrocompounds of toluene and/or naphthaline and/or diphenylamine.....	6-12
Vegetable meal.....	0-2

According to this definition gelatinous explosives can be made which closely approach the ordinary 65 per cent gelatine dynamite in strength, but have the great advantage over the latter of being absolutely non-freezing and being considerably safer in handling.

For example, the Gelatine-Astralit furnished by the Dynamit-Aktien-Gesellschaft vorm. Alfred Nobel and Company, much used in shaft sinking by the freezing process and also used in other rock work where non-freezing dynamite is desired in the colder parts of the year, such as in building water power plants, has about the following strength figures and composition:

Gelatinized dinitrochlorohydrine including nitroglycerine.....	30 per cent
Mixture of tri- and dinitrotoluene.....	10 per cent
Ammonium nitrate, sodium nitrate and wood meal.....	60 per cent
Lead block expansion.....	about 400.0 cc.
Lead block crushing.....	about 18.0 mm.
Sensitiveness.....	No. 3 Cap
Propagation in 25 mm. cartridges.....	20.0 mm.
Velocity of detonation.....	about 7300.0 m/s
Heat of explosion.....	1127.5 Cal.
Temperature of explosion.....	2534°C.
Density.....	1.45

The explosive is compounded on an oxygen balance, and so develops no injurious products of explosion.

On comparison with 65 per cent gelatine dynamite we have the interesting picture shown in table 45. From this it is evident that both explosives have about the same calculated brisance, which is confirmed experimentally by the lead block expansion.

Nitroglycol explosives²⁶

During the confiscation of glycerine for military purposes during the World War, nitroglycol was, as stated previously, used for a time to a certain extent in place of nitroglycerine, and in addition to the explosives mentioned on page 334 some have been made of mixtures of nitroglycerine and nitroglycol, particularly the 40 per cent dynamite and the so-called 18 per cent dynamite containing pure nitroglycol. On account of the extraordinary similarity of both explosive

²⁶ See Nitroglycol and Methylglycol Dinitrate in this chapter.

oils these do not differ in the least as regards explosive effects from the corresponding nitroglycerine explosives. The somewhat lower density of the nitroglycol as compared to nitroglycerine, or 1.5 vs. 1.6, is of no practical importance. The disadvantage of the higher volatility of the nitroglycol, the vapors of which produce headaches in sensitive persons, if they are inhaled carelessly in a closed room, has already been mentioned. On the other hand, the volatility is not so great as to lead to appreciable evaporation losses in packed (cartridged), gelatinous explosives and at normal storage temperatures.

Nitroglycol exudes from gelatines more easily than nitroglycerine. Therefore the collodion cotton content of the gelatine must be somewhat higher than when using nitroglycerine. On the other hand, the striking ease of detonation of nitroglycol allows the manufacture of a more solid gelatine. Whether or not the higher volatility and more ready exudation of nitroglycol from gelatines will allow transportation of these explosives to hot countries, as well as storage and use there, has not yet been determined.

The frequently mentioned Prussian police regulation of January 25, 1923, on the sale of explosives for mining purposes, allows according to section 11, which relates to brisant explosives for rock work, the complete or partial substitution of their nitroglycerine by other nitrated derivatives of glycerine or by nitroglycol. Only blasting gelatine is an exception to this. The reason for this is that a pure blasting gelatine consisting for example of nitroglycol and collodion cotton, has an oxygen deficiency and consequently develops carbon monoxide on explosion, which would be contrary to section 8 of the same Regulation according to which all explosives used in underground mining must be compounded on a theoretical oxygen balance or an oxygen excess. While nitroglycol itself has an exact oxygen balance and so decomposes into carbon dioxide, water vapor and nitrogen, the slight oxygen excess of nitroglycerine is sufficient, as is well known, to give a blasting gelatine having an oxygen balance when in the presence of the quantity of collodion cotton required for gelatinization. In gelatine dynamites containing nitroglycol the desired relations can naturally be obtained without difficulty by the oxidizing salts of the dope.

In addition to the property of not freezing at winter temperatures the nitroglycol explosives have the advantage of a lower sensitivity to mechanical effects and less tendency toward detonation on

ignition. A certain type is therefore permitted on the German railways in unlimited freight traffic under the name of "Gelatine-Astralit."

This Gelatine-Astralit should contain the following components:

	maximum
Gelatinized dinitroglycol.....	30
Aromatic dinitrocompounds.....	8
Aromatic trinitrocompounds.....	4
Ammonium nitrate and vegetable meal	

The explosive has the following characteristics:

Lead block expansion.....	415.0 cc.
Lead block crushing.....	19.0 mm
Sensitiveness.....	No. 1 Cap.
Propagation in 25 mm. cartridges.....	50.0 mm.
Velocity of detonation.....	about 6500.0 m/s
Density.....	1.45
Heat of explosion.....	1158.0 Cal.
Temperature of explosion.....	2485°C.
Gaseous products of explosion, at 0°, 760 mm. from 1 kg. explosive.....	884.4 liters
Specific pressure.....	8733.0 atm.

Therefore this explosive also attains almost the same strength as 65 per cent gelatine dynamite but is non-freezing, and as already mentioned, enjoys more favorable conditions on the railroads.

Gelatinous explosives very similar to the 40 per cent dynamite but with a higher content of nitroglycol and appreciably safer to handle, can be produced.

There has been no extensive introduction of the nitroglycol explosives, which are also permitted in France, since the World War, apparently on account of the high cost of manufacture of glycol.²⁷

²⁷ Ethylene glycol is now made in large quantities in the United States, as well as in Germany, and nitroglycol is used in explosives to a large extent. See previous note.

CHAPTER XXIII

NITROGLYCERINE EXPLOSIVES PERMISSIBLE IN GASEOUS AND
DUSTY MINES

Up until about forty years ago black powder and dynamite were the only explosives available to the miner for blasting coal and accompanying rock. Fire damp mixtures and coal dust clouds were readily ignited by both of these explosives. Only a fraction of a gram of the former (black powder) was required to ignite fire damp, or a few grams of dynamite, if exploded untamped in a borehole or in the open. Moreover coal dust clouds not containing admixed fire damp were ignited by small charges of black powder or dynamite (less than 100 grams), provided that the shot was from an untamped borehole.

Although this danger is less in actual practice, where shots are always made with tamped boreholes and ignition so requires larger charges, nevertheless blasting in coal mines has led to countless accidents, which can be traced largely to the ignition of fire damp or coal dust clouds directly by the action of the shot. In this connection the never-to-be wholly avoided blown-out shots were particularly dangerous. Such shots were encountered when the strength of the explosive was insufficient to loosen the burden, and the gases of explosion consequently blew out of the borehole at a high temperature, without being cooled down by any work performed.

These dangers and attendant accidents increased in proportion to the growth of the coal mining industry and as the mines became deeper and the amount of fire damp greater.

The ensuing demand from users of explosives to furnish explosives having a greater safety in fire damp, led in the course of the eighties of the previous century to the development of the so-called permissible explosives (permitted explosives, in England), which were established on both theoretical and practical bases.¹

¹ The expression is defined as Explosives Permissible in Gaseous and Dusty Mines (Permissible Explosives), since the designation "Safety Explosives (Sicherheitssprengstoffe)" can be confused with the term "Safety Explosives (to handle)" occasionally used. In France the expression is "Explosifs de

Attempts to produce coal and ore by purely mechanical means could not compete with blasting, on account of the increasing coal requirements of civilized countries. Also attempts which were made both before and during the development of permissible explosive to replace explosives known to be dangerous by processes depending upon chemical action, or to avoid the danger during firing by special precautions, led to no satisfactory results.

The chemical processes, which have only an historical interest and which were all complicated in manipulation, and inconvenient as well as uncertain and unsatisfactory in effects, are described by Heise with proper criticism.² The means which he described at the same place, of rendering blasting safer without regard to the nature to the explosive used, which in addition to the formation of a water curtain depended mainly upon the nature of the tamping, such as cartridges of water, tamping composed of salts containing water of crystallization or which would be volatilized, gave good results in part, with careful use, on account of the cooling of the gases of explosion. However, they were to a great extent dependent upon the care used and the reliability of the miner, and could not compete with the development of permissible explosives, which by their very nature offered a greater degree of safety and therefore became indispensable.

The theory of permissible explosives, as it has developed through knowledge and experience during the last forty years, was outlined in 1904 by Heise³ and more recently in a masterly way by Kast,⁴ so that it will suffice here to point out the factors especially important for the safety of explosives in fire damp and coal dust.⁵

The limits of explosion of mine-gas-air mixtures lie at about 5 to 14 per cent methane content of the air. The explosion is the most violent and propagates most easily at a methane content of 9.5 per

sûreté," in Belgium "Explosifs antigrisouteux" or "Explosifs S. G. P. (sécurité-grisou-poussière), in England "Permitted Explosives," in contrast to officially allowed "authorized explosives," and in the United States "Permissible Explosives."

² Heise, *Sprengstoffe und Zündung der Sprengschüsse*, Berlin, p. 60, Julius Springer (1904).

³ *Sprengstoffe und Zündung der Sprengschüsse*, p. 68.

⁴ *Spreng- und Zündstoffe*, (1921), p. 81.

⁵ See also Escalas, *Nitroglycerin und Dynamit*, p. 259.

cent, since then the oxygen present just suffices for combustion of the methane, thus giving the highest temperature of explosion. Since the temperature of ignition of the mixture is about 650 to 750°C., and the temperature of explosion of explosives considerably above 1000°C., ignition of the gas mixture by the explosion flame of the explosive could not be avoided unless, as Mallard and Le Chatelier have determined, there were a certain degree of delay in ignition, or a certain period of action of the high temperature required to cause ignition.

At 650°C. this period amounts to ten seconds, at 1000°C. to about one second, and at 2200°C. no delay is noticeable. The flame of explosion of brisant explosives is, however, of short duration and its high temperature endures only a small fraction of a second, since cooling begins immediately from the expansion and work done. This is the reason why black powder, with its slow decomposition and relatively long flame period always ignites mine gas-air mixtures.

Mallard and Le Chatelier looked upon the above temperature of 2200°C. as the limiting temperature in the sense that any explosive whose temperature of explosion was above this limit must ignite fire damp mixtures under all conditions.

The French Investigating Committee, created to study this question, considered the flame temperature of the shot as the essential cause of ignition of fire damp, and it was therefore decided in France that the essential characteristic of a permissible should be that its calculated temperature of explosion should in no case lie above 2200°C. Later this maximum temperature was fixed at 1500°C. for explosives permitted in coal seams and 1900°C. for accompanying rock.

Although these limiting temperatures based upon practical tests were on the whole correct, nevertheless such a conception of the permissible explosives was very one-sided. The unquestionably essential importance of the flame temperature is not limited to the real explosion temperature represented by the theoretical maximum case. Moreover, the quantity of explosive used is of considerable importance, since the flame increases with the quantity of the explosive and the actual temperature reached thus becomes higher, because the relative loss of heat to external objects decreases. The degree of safety in fire damp, determined practically in the so-called test gallery, shows that no explosive is absolutely safe, and that all of them can ignite fire damp if suitably large charges are exploded. This

determined the conception of the limit charge which is necessary to ignite the gas mixture with a given explosive.

The flame temperature can be kept low by:

1. The use of explosives having a low flame temperature, e.g., ammonium nitrate explosives.
2. By addition of such materials to the explosive which on explosion consume heat, either by evaporation or decomposition, and so reduce the flame temperature.
3. By limitation of the charge.
4. By converting the heat of explosion as completely as possible into work in the borehole by using proper tamping and arrangements of the shot, so that the explosion gases escape into the atmosphere in as cool a condition as possible.

The original French Investigating Committee took into consideration only the first two points. The importance of the third could only be recognized in practical studies of the question in the above-mentioned test galleries, and the fourth refers only to the use and not to the character of the explosive.

Furthermore, the length and duration of the flame of the exploding explosive has considerable influence on the flammability of the mine gas-air mixture. If the flame of an exploding cartridge is photographed in the dark it is found that the explosive which gives the largest flame photograph is less safe in fire damp, and that vice versa, permissible explosives give no flame photograph.

If the duration of flame stands in direct relation to the flame temperature in that at higher temperatures in general longer times are required to cool down the glowing gas particles and any solid products of explosion, on the other hand the composition of the products of explosion and the velocity of decomposition of the explosive are also of influence upon the duration of the flame.

Secondary reactions of the products of explosion between one another or with the air can prevent a sudden drop in temperature after explosion and so prolong the flame. This is the case when the explosive is compounded on an incomplete combustion equation and so evolves combustible gases such as carbon monoxide, hydrogen and methane, in addition to the usual carbon dioxide, water vapor and nitrogen. Moreover, the relatively slow release of oxygen from the alkali nitrates or alkaline earth nitrates, as compared to the explosive decomposition of ammonium nitrate, is capable of prolong-

ing the duration of the flame, which explains the unfavorable action of large additions of these nitrates upon the degree of safety of these explosives in coal dust. Such action can be limited by a favorable choice of other factors, such as low explosion pressure, as for example with Carbonites and Kohlencarbonites, which contain 25 to 35 per cent of potassium or sodium nitrate, and which were for a long time regarded as very safe and used to a great extent.

Taken by itself, as rapid and complete a decomposition of the explosive as possible in the sense of short flame duration, has a favorable effect upon the degree of safety in fire damp. However, a limit must be set on this in that raising the velocity of detonation raises the pressure simultaneously, and the flammability of the gas mixture increases with its compression. On the other hand, other factors in addition to the temperature of explosion raise the explosion pressure, such as density, velocity of detonation and quantity of gas, so that the total effective action of an explosive must not be exceeded if a high degree of safety in fire damp is to be attained.

This complication and only partial compensation of the various factors governing the matter of safety show the difficulty in the way of a theoretical consideration and calculation of the character and degree of safety of the various representatives of this class of explosives, as well as of various categories or types of the same.

Very soon all countries having coal mines turned to testing stations, maintained partly by private, partly by government funds, in which the explosive mixtures proposed as being safe in fire damp and coal dust were given practical tests. These artificial galleries had a portion partitioned off by a paper wall into a so-called explosion chamber, in which artificial mixtures of mine gas and air, or coal dust clouds, or both could be produced. The explosive to be tested was then fired from the bore of a steel mortar into test mixtures, and by graduating the quantity of the explosive there could be determined that charge which was just sufficient to ignite the flammable mixture, which could be observed through a heavy glass window. The next lower charge was designated as the "charge limit" at which the explosive was still safe. In this the most unfavorable conditions were intentionally chosen, more unfavorable than would subsequently be encountered as a general rule in practical use of the explosive in the mine, by allowing the explosive to act on the flammable mixture without tamping and without cooling the gases by performing work.

This introduced a certain factor of safety which would be expected to still make it safe with irregularities in blasting, such as shots blowing out without performing work, or on escape of uncooled gases through fissured rock. On the other hand, it is often customary, because of this severe test, to allow a certain increase in actual use over the limit charge determined in the test gallery.

Naturally the method of conducting such experimental work has considerable influence upon the results obtained, which however must always be regarded as relative. Differences in the method of testing have caused the various countries, although following the same principle in compounding the explosives in question and building up similar categories, to allow quite different strengths and kinds of permissible explosives. In Germany particularly there has been an effort to always make the method of testing free from set forms and thereby deepen them scientifically, by continually adjusting it to the peculiarities of the explosive, wherein naturally all factors which under unfavorable combinations could favor ignition and so increase the danger were taken into consideration.

Thus the greatest possible safety in mining is sought, and today this means that in spite of an enormous consumption of permissible explosives, amounting to several million kilos per year in the Ruhr field alone, fire damp and coal dust explosions traceable to proper use of proper permissible explosives no longer occur, while on the other hand the work done by these explosives has proven to be sufficient.

This has been attained without it being possible to give a sharp limitation on the term "Safety Explosives." The properties of the explosives, such as temperature of explosion, duration of flame, velocity of detonation and gas pressure are known to affect the safety. These must be combined with the fact that explosives to be designated as permissibles must possess a considerably increased degree of safety in fire damp and coal dust as compared to black powder and dynamite. The limit itself, and the test conditions under which an explosive should be tested and still considered a permissible, have remained in doubt, and as a matter of fact have been stated very differently at various times and in various countries.

A certain limit in this connection is drawn by the Prussian Ministerial Order of October 21, 1910, which states that the borehole charge in the mine may exceed by 50 per cent the safe limit found in the test gallery, if:

1. The explosive in question has been shown to be safe against fire damp and coal dust in the test gallery at a 250-gram charge.

2. No delay action firing is used.

3. The length of tamping is equal to half the depth of the hole.

4. The borehole does not have a larger diameter than 40 mm.

These regulations mean practically that the consumer will not use an explosive having a lower safety limit than 250-grams.

In German practice, however, a considerably higher safety requirement has grown up according to which explosives which have not stood the test with at least 500 grams, are difficult to introduce as permissibles.

The above-mentioned order has been replaced by the first list of mining explosives in the new police regulations published January 25, 1923, which determined for each permissible explosive the maximum charge allowed in mining, wherein it is a matter of charges of 600 to 800 grams, whereas the explosives in question gave a safe limit of 400 to 600 grams in the test gallery.

As regards the relation of results of the test gallery to actual practice, Heise⁶ recognizes that blasting in the mine is in itself less dangerous than the corresponding test in the test gallery, which latter is fired without tamping, performs very little work, and consequently allows the gases of explosion to act upon the flammable mixture at almost their initial temperature. However, blasting is not always done properly, so that it is impossible to estimate the relation and make the conditions in the test gallery comparable.

"The shot in the mine can be overloaded and prepared in such a way that it must act like a blown-out shot. If then the tamping is insufficient, or if it consists of dry coal dust, or if the charge of explosive fills the borehole too close to the mouth, it is easily possible that such a shot may be as great a source of danger as a blown-out shot in the test gallery. There should also be considered any possible, extraordinarily unfavorable local conditions, such as fissures in the rock, as a result of which the gases of explosion escape without performing any considerable work and the exploding material goes to waste, so to speak. The conditions are similar when the first of several shots partly or wholly moves the burden of the second.

Also it should not be assumed that the safe limit of an explosive determined in one gallery under certain conditions has a direct significance for all cases of practical mining operations. Only this can be said, that the permissible

explosive which in the test gallery was found to be particularly safe in fire damp in comparison to other explosives, is also safe to a high degree in practice.

In order to limit the danger in blasting in fire damp it is in any case right and proper to prescribe a maximum weight of the permissible charge and a minimum length of tamping."

At present the testing station of the Mining Association at Derne b. Dortmund is the standard and decisive bureau for Prussian mining, and it has been described at length by its manager, Bergassessor Beyling in *Glückauf*.⁷ The explosive industry has tried to adapt its own testing stations to this establishment and to also adopt their methods of testing.

Regarding these methods Beyling reports at length in *Glückauf*.⁸ An essential point is the cross sectional area of the gallery. The latter is elliptical, 183 cm. high and 132 cm. wide. The pressure developed in the explosion chamber by a given charge of explosive is naturally dependent upon the area of the cross section, for which reason the smaller, model galleries used by some explosives plants for test purposes use correspondingly smaller quantities of explosive, fired from a smaller mortar. The safe limits so obtained are of value only as a comparison, and it is necessary to compare simultaneously the safe limits of known permissible explosives for their evaluation for practical use.

The same thing applies when flammable mixtures of air and other gases or vapors, such as illuminating gas, benzine vapor, or petroleum ether vapor, are used for the test on account of lack of mine gas. Illuminating gas, on account of its content of readily ignited hydrogen, shows appreciably lower safe limits. Thus the vapor-air mixtures produced by atomization of benzine or better petroleum ether are always regarded merely as a help in case of need, since their composition at the instant of explosion is very difficult to determine and to a great extent dependent upon the operation of the spray heads, the temperature of the chamber and the iron walls of the gallery.

In this case also, the values obtained must always be compared with those given by known permissibles.

Methane produced artificially from aluminium carbide, always containing hydrogen, also gives results which are of only comparative

⁶ Heise-Herbst, *Bergbaukunde*, I, p. 217.

⁷ The Testing Station at Derne, Beyling and Zix, *Glückauf*, 49, p. 433 (1913).

⁸ *Glückauf* (1903), p. 435; (1907), p. 1142; (1908), p. 1717.

value for the same reason, unless the hydrogen has been previously completely removed by partial combustion.

If natural mine gas is available its methane content has a certain importance as regards the sensitiveness to ignition in that with mine gases of lower percentages the remainder of the gas frequently consists of air low in oxygen and thus consisting largely of inert gases, such as nitrogen and some carbon dioxide, so that a mixture prepared with 9 per cent CH_4 is then lower in oxygen than a similar mixture prepared by using a very high percentage mine gas.

Finally the specific case of the most dangerous mixture depends also upon the products of explosion, and thus upon the composition of the explosive. If the explosive on detonation gives an excess of free oxygen the limit of greatest sensitiveness to ignition of the gas mixture lies at a higher methane content than in the case of explosives burning incompletely and giving off carbon monoxide, which at least partly mixes with the explosive gas mixture, and so in an inverse sense displaces the relative oxygen content necessary for propagation of the gas explosion. Thus with combustible gases after explosion a too high methane content of the test mixture can show a greater degree of safety than is actually the case under unfavorable conditions, while with gases of explosion rich in oxygen a correspondingly high methane content merely represents the most unfavorable or most dangerous case.

In a severe test the most dangerous methane-air mixture for each explosive is sought, in order to construct the most dangerous condition conceivable in actual practice.

Insufficient consideration of these relations in the past led the German testing station usually to conduct the test of the explosive by shooting in a mine gas-air mixture containing about 8 to 9 per cent methane in which there was at the same time a cloud of coal dust, and thus in a primitive way try to imitate the conditions in the mine of simultaneous presence of fire damp and coal dust. Since most of the permissible explosives tested in Germany at that time were compounded on an incomplete combustion equation and gave off combustible gases of explosion, the flame of explosion and explosion pressure acted upon a mixture relatively poor in oxygen, which did not by any means represent the most dangerous case.

Beyling, manager of the Mining Association Testing Station then at Gelsenkirchen, now at Derne b. Dortmund, discovered these

relations in a very important, fundamental test in 1907-1908,⁹ and showed that most of the permissible explosives used at that time had a very small factor of safety in fire damp under the test conditions generally used, when they were fired into mine gas-air mixtures alone, without coal dust, while on the other hand they were comparatively safe when fired into coal dust. These two separate tests were therefore adopted generally in Germany, and were introduced in England some time later, where at first tamping was used in testing but later the more severe German method adopted.

This increased severity of the test at first caused considerable disturbance in the consuming and manufacturing fields, but it was soon discovered how to make explosives which would afford a high safe limit under the altered conditions, although this higher degree of safety brought with it quite generally a not inappreciable reduction in strength of the explosives.

The separate tests apparently corresponded better to conditions possible to encounter in practical mining operations, since accumulations of gas could very well occur, or gas pockets could be shot where no coal dust was present, as in work in accompanying rock, or where coal dust is wet on account of sprinkling and cannot be stirred up.

On the other hand the danger of coal dust can be present, or coal dust clouds can be stirred up by shooting, where no fire damp is present. This is the case in most of the coal fields of Upper Silesia, where fire damp is seldom encountered, and where only those explosive are desired which are safe in coal dust.

Although it is desired in testing to take into consideration the most dangerous possibilities of actual practice, it is impossible on the other hand to realize in every respect the conditions of practice when using the test gallery. While at the very first attempts were made to fire the explosive from a borehole in a clay or coal block, on account of the inconvenience and cost of constant work this was impossible, and moreover it would not have corresponded completely to actual conditions. For this reason the steel mortar was retained. The German test conditions have been drawn up to specify that the borehole of this mortar shall have a depth of 50 to 60 cm., and a diameter of 55 mm., the explosive cartridges being of the uniform diameter 35 mm. The cartridges are placed one behind the other in the borehole

⁹ Tests with Safety Explosives, *Gluckauf*, 1908, p. 1717+.

so that the innermost one rests against the bottom of the borehole, the upper cartridge being primed at the inner end by a blasting cap, which is fired electrically.

Thus the explosive does not fill the borehole, and is fired at a lower density of loading than in actual practice. For this reason the explosion pressure is less than in actual practice, which would correspond to a reduced severity of the test conditions as compared to actual practice. This defect, which is caused by the fact that no excessive demands can be made on the mortar without injuring it, are well counterbalanced by firing in turn without tamping, and allowing the gases of explosion to act directly upon the flammable mixture without doing work.

The objection that at lower densities of loading the decomposition of the explosive, and consequently the number of calories developed and the products of explosion, are different from those at high densities of loading, which in the case of explosives have a considerable oxygen deficiency cannot be left out of the consideration, has lost its significance, since it has been learned from other reasons and has become the custom to compound permissible explosives for complete combustion and even with an oxygen excess. In this case there is only one kind of decomposition possible, assuming a sufficient sensitiveness, and the calories and gases of explosion are independent of the densities of loading.

Moreover, the velocity of detonation, an important factor of brisance and consequently safety in mines, which is likewise affected by density of loading and kind of confinement, is less subject to this effect the higher the sensitiveness of the explosive to detonation. In this connection also it has been the effort, with some success, to use only explosives which react easily and surely to an initial impulse, and whose decomposition and velocity of detonation are not too much affected by the density of loading and degree of confinement. With these provisions the deviation of density of loading in the test versus that in practical use can be regarded as no particular defect of the method of testing, as many of the defenders of the French method claim. The latter, even today, place the main stress on the calculated temperature of explosion, and regard with skepticism the results of the testing station, on account of occasional abnormal phenomena not always explained.

Whether or not similar points of view can be brought up with regard

to the method long used in Austria at the testing station of the Segengottes Mine and at Mährisch-Ostrau, which detonates charges of explosive hanging in the flammable mixture without any confinement, appears somewhat doubtful. In this case the conditions differ greatly from actual practice, and although on the one hand the test is to be regarded as very severe, since the explosive acts directly on the flammable mixture without any loss of heat to any borehole wall, on the other hand only a few types of explosives detonate without any confinement whatever at the same velocity as in a borehole.

Of the factors which affect the results of the testing station the temperature of the gas mixture in the explosion chamber should not be left out of consideration. It is self evident that high temperatures favor ignition. It is therefore necessary to regulate the temperature in the interior of the gallery by heating with warm water or steam and to maintain it at about 28 to 30°C., corresponding to the temperature in deep mines.

In case of ignition of the gas mixture the temperature rises considerably from radiation of the heated gallery walls, and it is then ventilated for a long time by fans, in order to avoid any alteration in conditions of the test.

It is also evident that the kind and strength of the initiator used is not without significance, since the velocity of detonation and brisance are thereby affected. For this reason the strongest common cap, a No. 8, is chosen, in order to make the test conditions uniform. The lead azide caps in aluminium shells, recently come into wide use, give a somewhat greater initial impulse than the ordinary copper caps, which may well be due to the high temperature of combustion of the thin aluminium shell. This raises the gas pressure. In the determination of the lead block expansion of explosives by the Trauzl method this effect is felt considerably, and always gives an increase of about 15 per cent in the expansion, which is conceivable from the relation of the No. 8 blasting cap to the small, 10 gram cartridge. In tests with larger quantities of explosives, as in the crusher test with 100 grams, and determination of propagating powers, the influence of the aluminium cap is less, and it is only slightly felt in the permissible tests. With sensitive explosives having charge limits below 500 grams a displacement of the safe limit as a 50 gram reduction has been occasionally noticed with the aluminium cap as

compared to the copper cap. The testing station at Derne always uses aluminium caps.

Attempts have often been made to trace certain irregularities in the tests to atmospheric conditions and weather, even going to the trouble of making continual observations of air temperature, humidity and barometer to obtain data on such influences. Up to the present time no rule has been found, nor any scientific foundation for such phenomena.

MINE GAS SUPPLY AND ANALYSIS

Most testing stations have located in the vicinity of gaseous mines in order to have natural mine gas available, and lead the methane, which streams out of the so-called "blowers" in large quantities often for years through pipes to their gasometer, from which it passes via a gas meter into the explosion chamber of the gallery. In order to adapt their test conditions to those of the governing gallery explosives manufacturers have learned to do likewise. For example, the Nobel Company has had a compressor outfit for years at a coal mine, with which it compresses the mine gas from a "blower," supplied by contract, into 40-liter steel flasks at 150 atmospheres, and carries the methane in this compressed condition to their plant, which has a testing station corresponding to the one at Derne. The six cubic meters of gas obtained from such a flask supply about six test shots. The high cost of this experimental work due to such equipment and shipment of the steel flasks back and forth shows the care devoted by the explosives manufacturers to permissible explosives and the great importance of these studies to the explosives industry and mining in general.

In recent times a new, plentiful source of a constant supply of pure methane for the Derne gallery and for those of explosives manufacturers has been made available for use by the so-called Emscher Springs of the Emscher Company at Essen. These Emscher Springs form a part of the drainage clarification plant of the city of Essen. The sludge deposited in them evolves a mixture of pure methane and carbon dioxide, absolutely free from hydrogen and other disturbing gases. The gases are drawn off through collecting heads and passed at high pressure into steel flasks filled with water. The carbon dioxide is almost completely absorbed by the water, the methane only very slightly. The methane gas, freed from the carbon dioxide as described above, is compressed into steel flasks and taken to the testing station. On releasing the pressure from the flasks of water the carbon dioxide is given off, and they

then serve to free fresh quantities of gas from carbon dioxide without the use of chemicals.

Before each shot a sample of gas is removed from the explosion chamber, in which there has been a thorough mixing of the added gases for one or two minutes by means of a fan. The methane content is determined and any necessary addition of gas made on the basis of the analysis. The CH_4 determination is made either chemically by means of the Hempel explosion pipette¹⁰ or physically by a Zeiss refractometer or interferometer.¹¹ Both of the latter methods are relative, and for each new gas supply require a standardization of the apparatus based upon chemical analysis, since a content of foreign gases such as nitrogen or carbon dioxide can affect the refraction or interference figures.

Coal dust test

The fineness and gas content of a coal dust are very important factors in the flammability. Coal dust from a fat coal, very finely ground in a ball mill with iron balls, is used to test explosives in the testing station. The coal dust-air mixture is rendered more flammable by the presence of small quantities of mine gas, so small as not to be flammable in themselves, whereas highly flammable mine gas-air mixtures are rendered less flammable by admixture with coal dust because of the ensuing oxygen deficiency, which as already mentioned has led to a separate testing of explosives in mine gas and in coal dust.

Usually a few liters of coal dust are scattered on the bottom of the explosion chamber, and perhaps two liters more gradually introduced from above by the violent agitation of the fan. The whole is well stirred up. After a shot which fires the gallery a coking of the unburned particles of coal dust occurs, so the gallery is cleaned out and fresh coal dust scattered about so as to always maintain the same test conditions.

Among the factors which govern the safety of an explosive in fire damp and coal dust, brisance or explosion pressure plays a less important part in the question of coal dust than in fire damp. On the

¹⁰ Hempel, *Gasanalytische Methoden*, IV, p. 107 (1913).

¹¹ *Glückauf* (1913), p. 47.

other hand, the temperature of explosion and duration of flame are essential for the safety in coal dust.

Thus it happens that for example a dynamite, with its high explosion temperature, is just as dangerous in coal dust as in fire damp. On the other hand typical ammonium nitrate explosives, with their lower temperatures of explosion and shorter flames, are usually comparatively safe in coal dust, even at degrees of brisance which render them dangerous in mine gas. Alkali nitrates are substances which act unfavorably on the matter of safety in coal dust, since under certain conditions they give up their oxygen slowly and so prolong the flame.

In general, unless there are conditions present which are particularly favorable to coal dust ignition, the safe limits for coal dust-air mixtures are higher than for mine gas-air mixtures.

Under certain conditions this relation can be reversed, as Beyling has shown.¹² Explosives like carbonites, which are compounded on incomplete combustion equations and consequently develop considerable carbon monoxide and hydrogen on explosion, which are combustible gases, when fired from narrow boreholes or at high densities of loading, have ignited coal dust even at low charges, although they have a high degree of safety in fire damp.

Probably the combustible products of explosion as they escape from the borehole at a high pressure and temperature become ignited as they meet the air, and this secondary flame ignites the coal dust, whereas on the other hand on escaping into an air-methane mixture containing 8 to 9 per cent of the latter a relatively difficultly flammable mixture, poor in oxygen, is formed with the carbon monoxide and hydrogen. Coal dust-air mixtures and mine gas-air mixtures would according to this conception behave very differently toward the hot gases of explosion.

The German testing stations are in Derne (Mining Association Testing Station), Neunkirchen b. Saarbrücken (Government Testing Station), Aachen, Zwickau and Reuthen. Austria has a station at Mährisch-Ostrau (now Tschechoslovakia), Belgium one at Frameries.¹³ The French testing station at Liévin was destroyed during the war and built again at Montluçon. The English Official Testing

¹² Glückauf (1907), p. 1142.

¹³ For description see Watteyne and Stassart, *Ann. Min. Belgique*, X; Z. *Schiess- und Sprengstoffw.*, I, p. 135.

Station was originally at Altofts and was moved to Eskmeals in 1911.¹⁴ In the United States the testing station at Pittsburgh operates in connection with an experimental mine at Bruceston.

CLASSIFICATION OF PERMISSIBLE EXPLOSIVES

Every category of the brisant explosives can by a suitable gradation of brisance, by avoiding or limiting certain and adding other components, be rendered permissible.¹⁵ They are therefore recognized by the name of their most important component, such as permissible nitroglycerine explosives, or permissible ammonium nitrate, chlorate or perchlorate explosives. While permissible chlorate explosives were only used temporarily during the World War on account of the scarcity of saltpeter and glycerine at that time, and enjoyed a limited popularity,¹⁶ and perchlorate explosives were adopted to a certain extent, the permissible ammonium nitrate explosives are highly important and today play the principle part in coal mining.

In addition to this the permissible nitroglycerine explosives have had a prominent place from the very first, since on account of their high brisance they have maintained their position for the blasting of accompanying rock. They will be considered in the following. They can be divided into explosives having a base of liquid nitroglycerine, such as Wetterdynamit and Carbonit, and those having a base of gelatinized nitroglycerine, such as permissible gelatine dynamites. In Germany only the latter are in use today, the first group having become obsolete.¹⁷

By nitroglycerine explosives will be understood explosives with at least 20 per cent of nitroglycerine, those with a lower nitroglycerine content, as a rule 4 per cent, being considered in a special chapter,¹⁸

¹⁴ Now at Rotherham.

¹⁵ Kast (*Spreng- u. Zündstoffe*) also mentions on page 303 permissible explosives similar to black powder in his division of permissibles, and as a representative of this group gives on page 117 the English Bobbinite (62 per cent KNO₃, 17 to 19 per cent charcoal, 1.5 to 2.5 per cent S, 13 to 17 per cent ammonium sulphate and copper sulphate). However, such a powdered explosive would not meet the German requirements.

¹⁶ The chlorate explosives safe in coal dust played a certain rôle, however, in the coal mines of Upper Silesia, which were free from gas.

¹⁷ Both are no longer used in the United States.—TRANSLATOR.

¹⁸ See Chapter XXIV, Explosives Having a Low Nitroglycerine Content.

which also embraces the so-called semi-plastic type of permissibles with 10 to 12 per cent nitroglycerine, or in general the ammonium nitrate type.

COMPOSITION OF THE PERMISSIBLE NITROGLYCERINE EXPLOSIVES

Wetterdynamit

The oldest permissible explosives are the Nitroglycerine explosives, which were derived from guhr dynamite and the old wood meal, pulverulent dynamites. From the idea of using salts containing water of crystallization as tamping,¹⁹ the water of crystallization being evaporated by the hot gases of explosion and cooling the latter, it was only a step to mix these salts with the explosive itself.

Müller²⁰ and Aufschläger added crystals of washing soda, Epsom salt or Glauber salt in considerable quantities, and obtained an explosive having a high degree of safety in fire damp.

The original Wetterdynamit contained about:

	per cent
Nitroglycerine.....	42-52
Kieselguhr.....	11-13
Crystallized soda, magnesium sulphate or sodium sulphate....	47-35

An example of this, composed of 44 per cent nitroglycerine, 12 per cent kieselguhr, 44 per cent sodium sulphate, gave a lead block expansion of about 170 cc. and a lead block crushing of 10 mm. The effect is thus somewhat low as compared to the expenditure of nitroglycerine in the permissible gelatine dynamites in use today. Any efflorescence of the salts containing water of crystallization on long storage in dry air should be taken into consideration as regards change in the composition and properties of the explosive, i.e., increase in nitroglycerine content and diminution of the effective water content and consequently the degree of safety. Moreover the sulphates, on decomposition, give the gases of explosion a certain content of sulphurous acid or hydrogen sulphide if the kieselguhr is replaced by wood meal and an oxygen deficiency is present, as in the French and Belgian Grisoutit and Grisoutine. However, such Wetterdynamit was used for a long time, especially in Belgium and France. In

¹⁹ German patents 22006 and 103731.

²⁰ British patent 12424; Belgian patent 78865.

Austria this type was used until a few years ago with the composition: 52 per cent nitroglycerine, 14 per cent kieselguhr and 34 per cent soda crystals.

The Belgian Grisoutite or Grisoutine II has the composition: 44 per cent nitroglycerine, 44 per cent sodium sulphate or magnesium sulphate and 12 per cent cellulose or wood meal, and gives about 200 cc. expansion and 11 mm. crushing.

The corresponding French permissible dynamite had a quite similar composition. (See table 46).

In the United States these permissible dynamites were used at first under the designation Giant Coal Mine Powder and Giant Low Flame Powder and were given the generic name of "Hydrated Explosives."²¹

TABLE 46
Dynamite-grisoutite

	D	E
	per cent	per cent
Nitroglycerine.....	42	42
Magnesium sulphate.....	46	46
Wood meal.....	12	—
Kieselguhr.....	—	12

In addition to salts containing water of crystallization, salts were also used which gave off a large amount of gas on explosion and thus consumed heat, like bicarbonates and oxalates. In England particularly ammonium oxalate is very popular and still used today to a great extent in many explosives, whereas in Germany cheaper components or salt mixtures such as alkali chlorides, in connection with ammonium nitrate are preferred. An English permissible dynamite had the composition: 40 per cent kieselguhr dynamite, 45 per cent ammonium oxalate and 15 per cent sodium nitrate.

Carbonite

The carbonites, which likewise contain nitroglycerine in a liquid state and have the character of weak, mixed dynamites (not gelatines) were introduced by C. E. Bichel and furnished for a long time in

²¹ Also "N. G. Permissibles." TRANSLATOR.

large quantities. In Belgium a mixture of a composition corresponding to the Kohlencarbonit was sold as Colinite antigrisouteuse, Forcite antigrisouteuse, Minite and Sécurophore III. The carbonite type was also in use for a long time in England.

The Carbonitfabrik manufactured this dynamite up until shortly before the World War. It was characterized by a high degree of safety in fire damp and coal dust, attained by a very incomplete combustion with consequent low temperatures of explosion and low heats of explosion, and with a moderate strength. The main components were 25 to 30 per cent nitroglycerine, 25 to 35 per cent potassium or sodium nitrate, and spent tan meal, low grade rye flour or wood meal in quantities far too large for complete combustion by the saltpeter present.

The gaseous products of explosion of carbonite were therefore combustible and poisonous, and in addition to methane and hydrogen contained large amounts of carbon monoxide. In general high value is placed today on explosives for coal mining which give gaseous products free from carbon monoxide. A calculated oxygen balance in decomposition is now prescribed by the mine police in Germany. Meanwhile it has now been learned how, by suitable additions of vaporizable salts such as alkali chlorides in connection with ammonium nitrate, explosives having an oxygen balance and consequently complete combustion can be made with sufficiently low temperatures of explosion and a sufficient degree of safety in fire damp.

The use of such large quantities of edible meals as was customary in carbonites was moreover out of the question in Germany during and after the World War for economic reasons.

In the manufacture of these types meal and saltpeter, after a thorough drying and very fine grinding, were intimately mixed, and while in the mixer nitroglycerine added slowly in a fine stream. The most important representatives, according to Bichel,²² were as given in table 47.

The statements in the cited work of Bichel do not appear to be correct, and there seems to be no reason for the great deviations in data for very similar chemical compositions, for example for the relatively high temperature of explosion of Carbonit. Furthermore

²² Glückauf (1904), p. 1043.

the velocity of detonation of Carbonit II, with 30 per cent nitroglycerine, must be higher than that of Carbonit I, and not the reverse. The lead block expansions were determined by the older method of tamping with loam and compressing the block in a frame. According to the standards of the Fifth International Congress of Applied Chemistry at Berlin, sand tamping, which is in quite general use today, would give an expansion of the carbonites of only about 170 to 200 cc.

TABLE 47
German carbonites

	CARBONIT	KOHLEN-CARBONIT	CARBONIT I	CARBONIT II
	per cent	per cent	per cent	per cent
Nitroglycerine.....	25.0	25.0	25.0	30.0
Potassium nitrate.....	30.5	34.0	—	—
Sodium nitrate.....	—	—	30.5	24.5
Barium nitrate.....	4.0	1.0	—	—
Spent tan bark meal.....	40.0	1.0	—	—
Meal.....	—	38.5	39.5	40.5
Potassium bichromate.....	—	—	5.0	5.0
Soda.....	0.5	0.5	—	—
Heat of explosion in Calories per kilogram*.....	576	506	536	602
Temperature of explosion.....	1874°C.	1561°C.	1666°C.	1639°C.
Velocity of detonation in m/s....	2443	2700	3042	2472
Lead block expansion*.....	235 cc.	213 cc.	240 cc.	258 cc.

* Statements by Bichel, *loc. cit.*

The carbonites generally proved to be safe in fire damp at the highest charges used in the test gallery. On the other hand, their degree of safety in coal dust can be considered as problematical under certain conditions, on account of the combustibility of their gaseous products of explosion, particularly with the types which contain potassium nitrate. Potassium nitrate, even in permissible ammonium nitrate explosives, has proved to be a component which affects the safety in coal dust very unfavorably.

Permissible gelatine dynamite

The transition to permissible gelatinous explosives was by a carbonite in which the nitroglycerine was gelatinized by a little collodion

cotton. However, this had neither the form or density of a gelatine dynamite but was merely a crumbly, somewhat plastic mass, which was packed by hand or cartridged like guhr dynamite. Gelatine Carbonit Ia of the Carbonitfabrik contained 35 per cent nitroglycerine, 1 per cent collodion cotton, 17 per cent sodium nitrate, 36 per cent meal, 5 per cent common salt and 6 per cent glycerine-glue gelatine. The English representatives²³ of this class were as given in table 48. These explosives did not differ appreciably from the pure, powdery carbonites, and had the same advantages and defects, except in the case of Haylite I, which had a better combustion equation, but which would be considered as only moderately safe in fire damp and very safe in coal dust under German test conditions.

TABLE 48
English carbonites

	CARBONITE EXTRA	PHOENIX POWDER	HAYLITE NO. 1	OAKLITE NO. 1
Nitroglycerine.....	34.0-36.0	28.0-31.0	25.0-27.0	24.0-26.0
Nitrocellulose.....	0.1- 0.5	1.0	0.5- 1.5	0.5- 1.5
Potassium nitrate.....	24.0-27.0	30.0-34.0	19.0-21.0	32.5-35.5
Barium nitrate.....	3.0- 5.0	—	19.0-21.0	—
Wood meal.....	31.0-35.0	33.0-37.0	12.0-14.0	33.5-36.5
Gelatinized silicic acid.....	—	—	6.0- 8.0	—
Ammonium oxalate.....	—	—	10.0-12.0	—
Magnesium carbonate.....	—	—	—	0.5

GRISOUTINES

In France the carbonites are not allowed in coal blasting on account of their combustible vapors. As a result of the suggestion of the French Fire Damp Commission, which placed the major importance on a lower temperature of explosion, ammonium nitrate was added to the nitroglycerine explosives. The temperatures of explosion were calculated for mixtures of guhr dynamite and ammonium nitrate²⁴ and are given in table 49. Here, as already mentioned in the general section of this chapter, the influence of brisance upon ignition of the fire damp mixtures was not taken into consideration, so that accord-

²³ Other similar English explosives are given in Kast, *Spreng- und Zündstoffe*, p. 309.

²⁴ Escalas, *Nitroglycerin und Dynamit*, p. 267.

ing to the German ideas most of the French permissible explosives would not have a very high degree of safety on account of too high a brisance.

For example, a mixture of equal parts of guhr dynamite and ammonium nitrate, with a lead block expansion of 320 cc., in spite of its relatively low temperature of explosion, tested according to the German requirements, could not be considered as a permissible explosive.

There were manufactured in France the following so-called Grisoutines from gelatinized nitroglycerine and ammonium nitrate, containing a large oxygen excess, but only the 30 per cent belonged to the type of permissible explosives. On account of the low density of the ammonium nitrate the 30 per cent gelatine was not sufficient

TABLE 49

Temperatures of explosion for mixtures of guhr dynamite and ammonium nitrate

GUHR DYNAMITE	AMMONIUM NITRATE	TEMPERATURE
per cent	per cent	°C.
0	100	1130
20	80	1468
50	50	2090
100	0	2940

to so surround the salts as to make a mass which would cartridge well, and cartridging of this explosive is therefore very troublesome.

The French schedule and the long formalities of petition for official approval and changes allow a smooth adjustment of explosives to commercial requirements only with great difficulty. (See table 50.) At the present time the 12 per cent Grisoutines under the name of "Grisou Dynamite couche" are permitted in coal beds in France, and for rock work the 30 per cent Grisoutines under the name "Grisou Dynamite roche." According to the German test conditions the 30 per cent and 25 per cent Grisoutines would not be allowed as permissible explosives, the 20 per cent would give lower safe limits, and only the 12 per cent Grisoutine would be embraced within the range of permissible explosives used in this country.

Moreover the grisoutines must be regarded as irrational in composition on account of the lack of utilization of the ammonium nitrate as an oxygen carrier. The same strength can be attained with a

lower content of expensive nitroglycerine by partly replacing the latter by cheap carbonaceous ingredients. The increase in temperature of explosion caused by the combustion of the latter can in turn be regulated by suitable additions.

In Germany the development was from gelatinized carbonites, which were crumbly and little plastic, to the true permissible gelatine dynamites, in which the potassium or sodium nitrate was replaced by the more effective ammonium nitrate, with consequent increase in strength. At the same time the bulky carbonaceous ingredients were reduced, and to diminish the brisance and temperature of explosion increasing quantities of chlorides such as ammonium chloride and particularly potassium and sodium chloride were

TABLE 50
French Grisoutines

	12 PER CENT GRISOUTINE		20 PER CENT GRIS- OUTINE	GOMME DE SÛRETÉ	30 PER CENT GRISOUTINE	
	I	II			I	II
	per cent	per cent	per cent	per cent	per cent	per cent
Nitroglycerine.....	12.0	12.0	19.6	25	29.4	29.4
Collodion cotton.....	0.5	0.5	0.4	1	0.6	0.6
Ammonium nitrate.....	87.5	82.5	80.0	64	70.0	65
Potassium nitrate.....	—	5.0	—	10	—	5
Lead block expansion...	245 cc.	235 cc.	—	—	295 cc.	285 cc.
Lead block crushing.....	8.5 mm.	7.5 mm.	—	—	18 mm.	18 mm.

added.²⁵ At the temperature of explosive decomposition not merely the ammonium chloride, but also the alkali chlorides vaporize, the more completely the smaller their particle size, i.e., the finer they are ground. Their vaporization naturally reduces the temperature of explosion, but it should be noted that large additions of a chemically inactive material hinder the passage of the wave of detonation and consequently reduce the velocity of detonation and brisance. The alkali chlorides have proven to be the most effective and at the same time the most economical means of obtaining a high degree of safety in fire damp in all classes of permissible explosives, particularly in permissible gelatine dynamites.

²⁵ British patent 13531 (1903).

Bichel²⁶ recommended as particularly effective the addition of equivalent quantities of ammonium chloride and alkali nitrate, which would form alkali chloride in an extremely fine state of subdivision, or in the most effective form, and at the same time combine the hydrochloric acid set free from the ammonium chloride with a metal and remove it as such from the products of explosion.

Other chlorine compounds in connection with alkali nitrates were also proposed for this purpose.²⁷ However, the mere addition of alkali chloride was finally found to be just as effective and the most economical.

In England the oxalates were preferred for obtaining the same result, mainly ammonium oxalate, which is still used to a large extent today in the permissible nitroglycerine explosives. In Germany actual experience has shown the more expensive oxalates to have no technical advantage over the alkali chlorides used for the same purpose.

A further step in the development of permissible nitroglycerine explosives was the adaptation of their form, density and plasticity to that of the true gelatine dynamites. The explosives previously described were more or less pulverent and lacked the advantage of high density and plasticity of gelatine dynamites, which would spread out against the walls of the borehole. Since the nitroglycerine content of the permissible explosives naturally has to be held to certain limits so that their brisance will not be too high to give high charge limits, the plasticity had to be increased by adding certain materials, because the quantity of nitroglycerine-gelatine present was usually insufficient to hold the solid components as a cohesive, plastic, flexible mass. The technical term for this was "lengthening or stretching the gelatine." These added materials were important from the commercial and manufacturing point of view as affecting the ease of cartridging. A sufficiently soft, plastic mass can be easily packed on the same cartridge machine as ordinary gelatine dynamite, whereas plastic gelatines with a low nitroglycerine-gelatine content can under certain conditions form so stiff a mass that their cartridging is an extremely difficult matter, especially after they have become cold or been stored.

²⁶ German patent 175391 (1902); British patent 28245 (1902).

²⁷ British patent 5791 (1903); trichloroacetates and alkali nitrates.

Aside from such special additions the collodion cotton content of the gelatine plays a very important rôle, as has already been pointed out under gelatine dynamites. Softer gelatines with a lower collodion cotton content can be cartridged better than those which are stiffer from more collodion cotton.

Furthermore the content of voluminous components such as wood meal, plays a very important part in the question of plasticity and ease of cartridging. This component must usually be held within rather narrow limits, depending upon the nature of the explosive.

For the "stretching" of the gelatine mainly such components are used as will dissolve in nitroglycerine and thus form a homogeneous mass with it, like aromatic nitrocompounds and aromatic hydrocarbons, e.g. naphthalene. In the case of explosives which have a nearly complete combustion equation and good fumes on explosion, such added compounds do not act favorably on the permissibility, since the temperature of explosion is naturally raised considerably.

Also liquids insoluble in nitroglycerine, and heterogeneous gelatines used as such additions, when in a state of fine subdivision in the explosive or emulsified with the nitroglycerine, are capable of increasing the plasticity of the explosive in the manner desired. For example, the Carbonitfabrik made considerable use of a glue-gelatine called "Melan," a jelly obtained by boiling glycerine with an aqueous solution of glue, for increasing the plasticity. The Dynamit A.-G. vormalis Nobel & Co. added substances wholly or partly soluble in water or which swelled up with water, such as dextrine, starch or gums, to the nitroglycerine-gelatine.²⁸ Potato flour increases the plasticity in the same way.

Also pure glycerine, a so-called gum-sugar or a syrupy, concentrated sugar solution which would not crystallize, small amounts of vegetable oils, or liquid hydrocarbons such as paraffin oil, were added for the same purpose. Such oils when present in too large quantities can affect the sensitiveness and propagation, even of nitroglycerine explosives. Also concentrated waste sulphite liquors²⁹ have been found to be very suitable for stretching the gelatine.

In contrast to all the above substances, which are carbonaceous materials and consequently require oxygen for combustion, and raise

TABLE 51
Composition of permissible gelatine dynamites

	GELATINE-CARBONIT	NOBELIT	FÖRDIT	FÖRDIT I
	per cent	per cent	per cent	per cent
Nitroglycerine.....	25.3	28.0	23.00	25.5
Collodion cotton.....	0.7	0.7	0.98	1.5
Nitrotoluene.....	—	—	3.50	5.0
Glue-gelatine.....	6.9	—	—	—
Glycerine.....	—	—	8.70	3.0
Dextrine.....	—	2.5	0.72	4.0
Potato flour.....	—	10.0	—	—
Vegetable oil.....	—	0.5	—	—
Wood meal.....	—	1.0	—	—
Ammonium nitrate.....	41.5	39.7	41.00	37.0
Sodium chloride.....	25.5	17.6	—	—
Potassium chloride.....	—	—	22.00	24.0
Ultramarine.....	0.1	—	—	—
"Bolus" (china clay).....	—	—	0.10	—
Lead block expansion.....	260 cc.	270 cc.		
	SAFETY JELLY DYNAMITE	PERMISSIBLE GELATINE DYNAMITE		
		Ia	I	III
	per cent	per cent	per cent	per cent
Nitroglycerine.....	32.25	38.0	40.0	28.0
Collodion cotton.....	1.25	1.0	1.0	0.7
Glue-dextrine-glycerine jelly.....	9.60	—	—	—
Dinitrotoluene.....	—	—	—	11.0
Rye flour.....	18.00	14.0	10.0	4.0
Wood meal.....	—	—	2.0	—
Liquid hydrocarbon.....	—	4.0	3.5	—
Ammonium nitrate.....	22.60	25.5	27.0	37.0
Sodium nitrate.....	10.80	—	—	—
Potassium nitrate.....	—	5.0	4.0	—
Common salt.....	—	—	—	19.3
Potassium chloride.....	5.50	—	—	—
An oxalate.....	—	2.5	—	—
A fatty acid salt.....	—	10.0	12.5	—

²⁸ German patent 182030 (1903), so-called "Nobelit Patent."

²⁹ German patent 353200.

the temperature of explosion, the Dynamit A.-G. has recently used accurately measured quantities of saturated solutions, particularly a somewhat syrupy, saturated calcium nitrate solution,³⁰ which is in itself an oxidizing material. It imparts to the explosive a high degree of plasticity without affecting the sensitiveness by the attendant water content. It allows the manufacture of gelatinous explosives of low nitroglycerine content which cartridge well, have an oxygen excess and high charge limits, and has recently been used to a large extent, for example in the Wetter-nobelites, etc.

Table 51 gives the older representatives of such permissible gelatine dynamites.³¹ These explosives are cohesive masses of high density, similar to gelatine dynamites. In the case of the Gelatine-carbonit the density amounts to 1.6. The combustion equation is usually more favorable than in the case of the carbonites, although with most of them the gases of explosion still contain some carbon monoxide. Only the gelatine-carbonite was compounded on an approximate oxygen balance. Their higher strength as compared to the first permissible dynamites and carbonites is worthy of notice. However, it was found after some time by means of a change in the conditions of the test³² that such strong explosives had only a low degree of safety in mine gas-air mixtures, since by the German method they were tested in mine gas alone, without admixture of coal dust, whereas their degree of safety in coal dust alone was always satisfactory. They therefore disappeared after the 1909 investigation by Beyling previously mentioned, and were replaced by the less brisant mixtures which satisfied the new test conditions.

In England the earlier methods of testing at the Woolwich Station led to even more brisant permissible explosives, which in part did not differ appreciably from ordinary gelatine dynamites and in part approached the German low-strength substitute dynamites.³³

The fundamental difference between the older English method of testing and the Continental method was that in England the shots were fired from a tamped mortar, while on the Continent only the results from an untamped mortar were taken into consideration. It was assumed that in actual practice only well tamped shots would

³⁰ German patent 349166 (1919) and Addition 372506,

³¹ *Glückauf*, II, p. 1717+ (1908).

³² See introduction to the chapter.

³³ Bichel, *Z. Schiess- u. Sprengstoffw.*, II, (1907), p. 170+.

be fired and that therefore the results of untamped shots need not be considered. At that time exceptional conditions and particularly unfavorable circumstances were not taken into consideration. Reference should be made in this connection to the above-mentioned investigations by Heise.

According to English regulations the tamped shots were fired from a mortar into a mixture of 15 per cent illuminating gas and 85 per cent air, the diameter of the gallery being 72 cm. The requirement

TABLE 52
List of English permissible explosives

	RIPPITE	SAXONITE	GELTITE	RUSSELTITE	CORONITE
Nitroglycerine.....	59.5-62.5	42.5-62.0	56.0-59.0	40.0-42.0	38.0-40.0
Nitrocellulose.....	3.5-4.5	2.5-5.0	2.0-3.5	1.75-2.75	0.8-1.3
Potassium nitrate.....	18.0-20.0	16.0-27.5	17.0-21.0	24.0-26.0	3.0-5.0
Ammonium nitrate.....	—	—	—	—	26.0-28.0
Wood meal.....	3.5-5.5	3.5-8.0	8.0-9.0	3.0-5.0	2.0-4.0
Cereal meal.....	—	—	—	—	8.0-11.0
Chalk.....	—	0.5	—	0.5	—
Castor oil.....	0.5-1.5	—	—	—	—
Ammonium oxalate.....	9.0-11.0	9.0-27.0	11.0-13.0	22.0-24.0	—
Aluminium stearate.....	—	—	—	—	11.0-14.0
Liquid hydrocarbon.....	—	—	—	—	2.0-4.0

The wide limits in the various components of the prescribed composition are astonishing, since on the Continent at that time only explosives of exactly defined percentage composition, for example in Germany defined on the basis of the so-called Blasting Lists of officially recognized testing stations, were allowed by the authorities to be used in coal mines. The Prussian Mining Police Regulation, for example, permits of only a deviation of 0.5 per cent in the various components from the quantities appearing on the Blasting Lists.

was that of twenty shots with a quantity which gave a certain recoil of the ballistic pendulum,³⁴ with tamping 12 and 9 inches long, no shots should fire the gallery. Coal dust was not considered. With this method the smaller gallery diameter and high sensitiveness to ignition of the illuminating gas mixture gave a severe test, while on the other hand the tamping diminished appreciably the ease of ignition. Also the amount of charge was not especially high. Nothing was said about determination of charge limit.

³⁴ Guttman, *Industrie der Explosivstoffe*, p. 623.

This method caused only the most extreme explosives such as unchanged, pure, highly brisant dynamites on the one hand and those similar to black powder on the other hand, to ignite the gallery. At the highest brisance and very high temperature ignition occurred in spite of tamping, while the flame of black powder was of such long duration that it ignited the mixture after the tamping had been blown away.

Those between these extremes did not cause ignition on account of the tamping, and were formerly considered as permissible explosives in England. Even Bobbinite,³⁵ a black powder explosive whose flame was reduced by the addition of ammonium sulphate, was for a long time regarded as a permissible and suitable for coal mines, although it did not differ essentially from black powder and was anything but safe in fire damp and coal dust, and it has perhaps been the cause of numerous accidents.

Only a few examples of explosives which were at that time regarded as permissible in England, appearing as such on the "Special List" of the so-called "Permitted List" since 1900, will be given here. (See table 52.)

Later the English test regulations were brought into conformity with the Continental method and every explosive similar to dynamite taken off the Permitted List. For shooting in coal today in England pulverent ammonium nitrate explosives containing some common salt and a moderate proportion of nitroglycerine, perhaps 10 to 15 per cent, are mostly used, which are also permissible according to German ideas and which will be mentioned in the next chapter.³⁶

PERMISSIBLE GELATINE DYNAMITES FROM 1908-1914

Some examples of permissible gelatine dynamites as made and tested in Germany according to the new, separate testing in mine gas and coal dust are as shown in table 53. Of very similar composition were Gelatine-Sonnit,³⁷ Neu-Romperit,³⁸ Saxonit,³⁸ Gesilit,³⁹ Gela-

³⁵ See Kast, *Spreng- und Zündstoffe*, p. 303.

³⁶ See Part III, Chapter XXIV, Explosives with a Low Nitroglycerine Content.

³⁷ Deutsche Sprengstoff-A.-G. Hamburg.

³⁸ Dresdener Dynamitfabrik.

³⁹ Sprengstoffwerke Dr. R. Nahnsen & Co.

TABLE 53
German permissible explosives

	NEU-NOBELIT I*	NEU-NOBELIT XII*	NEU-NOBELIT XIV*
	per cent	per cent	per cent
Nitroglycerine-gelatine.....	26.0	30.0	30.0
Dinitrotoluene.....	8.0	—	—
Gum-sugar.....	—	3.5	—
Potato or grain flour.....	9.0	—	6.4
Wood meal.....	1.0	—	—
Ammonium nitrate.....	27.0	36.0	30.5
Common salt.....	29.0	30.5	33.1
Oxygen balance.....	-14.9%	+4.6%	-1.6%
Lead block expansion.....	230.0 cc.	220.0 cc.	230.0 cc.

	GELATINE- CARBONITE I†	GELATINE- CARBONITE D†	FÖRDIT IV‡	AGESID 2‡
	per cent	per cent	per cent	per cent
Nitroglycerine-gelatine.....	23.6	30.0	22.0	30.0
Trinitrotoluene.....	3.0	—	—	—
Nitrotoluene.....	—	—	5.0	—
Glycerine.....	4.0	2.5	3.0	—
Vegetable Jelly.....	—	—	—	2.0
Wood meal.....	—	—	—	1.0
Cereal or potato flour.....	10.0	—	12.0	—
Sodium nitrate.....	4.4	—	—	—
Potassium nitrate.....	—	5.1	—	—
Ammonium nitrate.....	31.0	31.5	38.0	36.0
Common salt.....	24.0	30.9	—	—
Potassium chloride.....	—	—	19.0	31.0
Ammonium oxalate.....	—	—	1.0	—
Oxygen balance.....	-13.1%	+5.3%	-19.5%	+5.0%
Lead block expansion.....	220.0 cc.	225.0 cc.	220.0 cc.	225.0 cc.

* Dynamit A.-G. vorm, Alfred Nobel & Co.

† Sprengstoff A.-G. Carbonit.

‡ A.-G. Siegener Dynamitfabrik.

tine-Siegenit,³⁹ Anzit,³⁹ Gelatine-Dahmenit⁴⁰ and Gelatine-Leonit.⁴⁰ This group also includes the permissible gelatine dynamites of the Westfälisch-Anhaltische Sprengstoff A.-G., Berlin, for example No.

⁴⁰ Westdeutsche Sprengstoffwerke A.-G.

28 of the following composition: Nitroglycerine-gelatine, 30 per cent; naphthaline 1.5 per cent; ammonium nitrate, 33.5 per cent; potassium chloride, 35 per cent; oxygen balance, +2.2 per cent; lead block expansion, 220 cc.

During the years of the World War the German coal mines were furnished only very small quantities of these plastic permissible explosives of a comparatively high nitroglycerine content. The confiscation of glycerine, and its almost exclusive use for military purposes allowed mining to have only the most necessary quantities of nitroglycerine, so that the high percentage, highly brisant nitroglycerine explosives were used only at places where their use was indispensable for rational mining. This was the case, for example, in iron ore and iron pyrites mines, while other mining operations and stone quarries, aside from the liquid air process used particularly in limestone, turned almost exclusively to chlorate explosives. Permissible chlorate explosives were also made and used for a short time in coal mining, but they met general suspicion on account of their intense flame, so that they soon disappeared from coal mines, although they caused no noticeable accidents, and a quantity of ammonium nitrate was released to provide the mines with ammonium nitrate explosives. This branch of mining shifted for several years to ammonium nitrate explosives containing 4 per cent nitroglycerine, which proved to be sufficient for coal mining but often too weak for blasting accompanying rock.

On release of glycerine after the war a strong demand for stronger and denser explosives for coal mining arose, and although for work in the coal the ammonium nitrate explosives were largely retained,⁴¹ on the other hand the consumption of permissible gelatinous explosives containing 25 to 30 per cent nitroglycerine for work in accompanying rock increased from year to year.

A series of new explosives was tested by the testing stations, mainly the one at Derne, and introduced. They were like the type used in the last few years before 1914. However, it had meanwhile become a rule to use for underground work only explosives compounded on complete combustion equations or having an oxygen excess, so that the fumes would be free from carbon monoxide. This has since been

⁴¹ In the Ruhr coal field the Wetter-Detonites of the Dynamit A.-G. vorm. A. Nobel & Co., and the Wetter-Westfälites of the Westfälisch-Anhaltische Sprengstoff-A.-G. are used to a great extent today.

made a law.⁴² The consequent relatively high temperature of explosion must be equalized by corresponding additions of salts to reduce the temperature of the gases of explosion and the total strength, and safety with maximum charge limit is only attained by explosives of moderate brisance, and a lead block expansion of 200 to 220 cc.

With the usual nitroglycerine content of 25 to 30 per cent which in general should not be exceeded for economic reasons and for the greatest possible safety in fire damp, the "stretching agents" for gelatine seem still indispensable to render the gelatine flexible and capable of cartridging well. Such substances as cereal meals, potato flour, and sugar syrup important for human or animal consumption, were eliminated even after the war for reasons which can well be understood. Others, such as glycerine, which were in themselves very suitable, were given up on account of their high cost or else used to only a limited extent. In any case, the use of glycerine in the manufacture of explosives is more economical in the form of nitroglycerine.

In place of such materials the cheap vegetable glue, cheap cellulose-pitch-syrup⁴³ and saturated calcium nitrate solution preferred by the Dynamit A.-G.,⁴⁴ are used, the latter being at the same time an oxidizing agent and particularly suitable for the manufacture of explosives having an oxygen excess.

Aromatic nitrocompounds as "stretching agents" for gelatines raise the heat of explosion considerably, and require a corresponding diminution of brisance by addition of correspondingly increased quantities of salts to afford a proper degree of safety. An example of such explosives is Gelatine-Carbonit 30, having the composition: Gelatinized nitroglycerine, 30 per cent; nitronaphthaline, 3 per cent; ammonium nitrate, 24 per cent; potassium nitrate, 2 per cent; potassium chloride, 41 per cent; having an expansion of 210 cc. and approximately an oxygen balance.

On the other hand, the Nobelites 18 to 23 of the Dynamit A.-G. contain 2 to 5 per cent of a saturated calcium nitrate solution and, some dinitrotoluene as "stretching agents." Altogether they show

⁴² Prussian Police Order of January 25, 1923, §§ 8 and 18, see Reichsanzeiger, 1923, No. 41, Supplement 1.

⁴³ German patent 353200 to Dyn. A.-G. and Dr. Naoum.

⁴⁴ German patent 349166 and Addition 372506 to Dynamit. A.-G. and Dr. Naoum.

TABLE 54

Mining list published in the Reichsanzeiger

NAME	CHEMICAL COMPOSITION	COMPANY AND PLANT	MAXIMUM CHARGE	
			For gaseous mines	For non-gaseous coal mines
Wetter-Nobelit A	per cent 26.00 gelatinized nitro-glycerine 2.50 Ca (NO ₃) ₂ solution 32.00 NH ₄ NO ₃ 2.00 Dinitrotoluene 1.00 Wood meal 36.50 Common salt	Dynamit A.-G., vormals A. Nobel & Co., Hamburg, Schlebusch Plant	800	800
Wetter-Nobelit B	30.00 gelatinized nitro-glycerine 3.00 50 per cent Ca(NO ₃) ₂ solution 26.50 NH ₄ NO ₃ 0.50 Wood meal 40.00 Common salt	Same	800	800
Wetter-Nobelit C	24.70 gelatinized nitro-glycerine 5.00 Ca(NO ₃) ₂ solution 29.30 NH ₄ NO ₃ 2.00 Dinitrotoluene 1.00 Wood meal 38.00 Common salt	Same	800	800
Wetter-Carbonit A	Identical with Wetter-Nobelit B	Carbonit A.-G. Hamburg, Schlebusch Plant	800	800
Wetter-Agesid A	30.00 gelatinized nitro-glycerine 27.00 NH ₄ NO ₃ 3.40 Sodium nitrate 1.60 Magnesium silicate 38.00 Potassium chloride	A.-G. Siegerner Dynamit Plant Köln, Förde Plant	800	800

TABLE 54—Concluded

NAME	CHEMICAL COMPOSITION	COMPANY AND PLANT	MAXIMUM CHARGE	
			For gaseous mines	For non-gaseous coal mines
Wetter-Markanit A	Identical with Wetter-Nobelit A	Westdeutsche Sprengstoff A.-G., Dortmund, Rummenohl Plant	800	800
Wetter-Wasagit A	per cent 28.00 gelatinized nitro-glycerine 1.00 "Gelose" 20.00 NH ₄ NO ₃ 10.00 Ba(NO ₃) ₂ 0.50 Talc 40.50 Potassium chloride	Westfälisch-Anhaltische Sprengstoff A.-G., Berlin (a) Sythen Plant, (b) Reinsdorf Plant	800	800
Wetter-Wasagit B	26.00 Gelatinized nitro-glycerine 36.00 NH ₄ NO ₃ 1.35 Trinitrotoluene 1.35 Dinitrotoluene 0.30 Wood meal 35.00 Potassium chloride	Same	600	800
Wetter-Arit A	25.00 Nitroglycerine 0.80 Collodion cotton 1.00 Glycerine 29.50 NH ₄ NO ₃ 3.70 Trinitrotoluene 40.00 Sodium chloride	1. Bayerische Sprengstoffwerke u. Chemische Fabriken A.-G. Nürnberg, Neumarkt Plant. 2. Deutsche Cahuëitwerke A.-G. Gnaschwitz, Gnaschwitz Plant	700	800
Wetter-Arit B	25.00 Nitroglycerine 0.80 Collodion cotton 1.00 Glycerine 31.00 NH ₄ NO ₃ 4.20 Trinitrotoluene 38.00 Sodium chloride	Same, Neumarkt Plant Gnaschwitz Plant	800	800

3 to 5 per cent oxygen excess. In the last few years the Ruhr District has consumed large quantities of these, particularly the Nobelit 19, which has the following composition:

TABLE 55
Explosive data of the Wetter-Nobelites

	WETTER-NOBELITES		
	A	B	C
Oxygen balance.....	+4.1	+6.1	+4.2
Lead block expansion.....	215.0 cc.	205.0 cc.	205.0 cc.
Lead block crushing.....	14.6 mm.	12.0 mm.	12.1 mm.
Sensitiveness.....	Cap No. 1	Cap No. 1	Cap No. 1
Density.....	1.8	1.7	1.7
Velocity of detonation.....	4200 m/s	4880 m/s	3050 m/s
Heat of explosion.....	589 Cal.	513 Cal.	545 Cal.
Temperature of explosion.....	1820°C	1688°C.	1727°C.
Charge limit* (fire damp).....	600.0 grams	650.0 grams	700.0 grams
Charge limit* (coal dust).....	700.0 grams†	700.0 grams	700.0 grams

* According to determination in the Derne Testing Station.

† Higher charges than 700 grams were not used at Derne.

	per cent
Gelatinized nitroglycerine.....	26
Saturated calcium nitrate solution.....	5
Dinitrotoluene.....	2
Wood meal.....	1
Ammonium nitrate.....	34
Common salt.....	32
Lead block expansion.....	220.0 cc.
Lead block crushing.....	14.0 mm
Velocity of detonation.....	3750.0 m/s.
Oxygen balance.....	+5.0%
Density.....	1.75
Heat of explosion.....	575.0 Cal.
Temperature of explosion.....	1750°C.

The large number of permissible explosives tested, offered and sold by the various companies under the most varied, phantastic names has recently suffered a reduction by a new ministerial regulation of the whole field of explosives, at least for Prussian mining, in that according to the police regulation of January 25, 1923, coming into effect January 1, 1924, only those explosives shall be offered for sale to

mines which have been shown on the issued "List of Mining Explosives" of the Prussian Minister of Commerce and Labor, and made by the companies shown in this list as manufacturing such individual explosives. Moreover, the explosives must satisfy the provisions of the police regulation in question and be specially approved by the Chief Mining Council in whose district they are to be sold.

The first mining list published in the *Reichsanzeiger* conforming to the above police regulation contained the gelatinous explosives shown in table 54.

The explosive data of the Wetter-Nobelites, of which the type A has been largely used for a long time are given in table 55.

Non-freezing permissible explosives

Some of the types previously mentioned should be included in the group of low-freezing permissible nitroglycerine explosives. They contain nitrotoluene or dinitrotoluene⁴⁶ in quantities of about 20 per cent that of the nitroglycerine, or about 5 to 6 per cent nitrotoluene to 25 to 30 per cent nitroglycerine. A gelatinous Nobelit type containing nitrotoluene belongs to the period before 1908.⁴⁶ The Austrian Pannonit falls in this group.⁴⁷ There are also the so-called non-freezing Nobelites in which 20 per cent of the nitroglycerine has been replaced by dinitrochlorohydrine, and these likewise correspond to the older types of Nobelites.⁴⁸

Non-freezing gelatinous permissible explosives based on dinitrochlorohydrine, with a low content of nitroglycerine (so-called nitrochlorin) were known under the designations of Gelatine-Wetter-Astralit and Gelatine-Prosperit. The latter, for example, has the composition shown in table 56. The field of application of such explosives is limited for two reasons. In the first place coal mining is below ground, and its explosives are stored there, or out of reach of frost, so that the demand for non-freezing permissible explosives is not particularly great. Moreover, explosives which have frozen during transportation in the cold parts of the year have an oppor-

⁴⁶ See Chapter XXII on Non-Freezing Nitroglycerine Explosives.

⁴⁷ Kast, *Spreng- und Zündstoffe*, p. 311, Permissible Gelatine Dynamites, Gesilites and Fördites with Nitrotoluenes. These belong in part to the older type and today are no longer regarded as safe.

⁴⁸ Kast, p. 313.

⁴⁹ Kast, p. 312.

tunity to thaw gradually at the warm temperature of most explosives magazines located at considerable depths below ground. On the other hand, dinitrochlorohydrine is more expensive than nitroglycerine, so that such explosives, in view of their higher price, are only demanded where their non-freezing properties are particularly important.⁴⁹

The original idea that dinitrochlorohydrine would be particularly suited for the manufacture of explosives which were very safe in gaseous and dusty mines, due to its lower temperature of explosion than nitroglycerine, and the formation of common salt in a nascent

TABLE 56

Composition of Gelatine-Wetter-Astralit and Gelatine-Prosperit

	I	II
	per cent	per cent
Dinitrochlorohydrine.....	20.0	20.0
Nitroglycerine.....	5.0	5.0
Collodion cotton.....	0.5	0.5
Dinitrotoluene.....	5.0	5.0
Meal.....	2.5	2.0
Ammonium nitrate.....	36.0	30.0
Sodium nitrate.....	4.0	10.0
Common salt.....	21.0	27.5
Potassium oxalate.....	6.0	—
Expansion.....	225.0 cc.	210.0 cc.
Oxygen balance.....	+0.4%	-1.2%
Charge limit.....	600.0 grams	700.0 grams

state in the presence of saltpeter, has not been confirmed. These peculiarities are readily effaced by the rest of the make-up of the explosive, and explosives which are just as safe can be made with nitroglycerine.

The same thing applies to the non-freezing gelatinous explosives which are permissible and based upon the use of dinitrolycerine, which were supplied for a long time by the Rummenohl Plant of the Westdeutsche Sprengstoffwerke of Dortmund under the names of Tremonit, Gelatine-Dahmenit and Gelatine-Leonit.

⁴⁹ In the future dinitrochlorohydrine will probably be replaced by nitroglycol in this type of explosives also.—AUTHOR.

The Tremonites, which sprung up in the period before 1908 and which today are no longer regarded as sufficiently safe, had the composition⁵⁰ given in table 57. The Gelatine-Dahmenites have

TABLE 57

Composition of the Tremonites

	TREMONTES		
	S	SI	SII
	per cent	per cent	per cent
Gelatinized dinitrolycerine.....	36.0	36.0	34.0
Trinitrotoluene.....	—	—	2.5
Wood meal.....	1.7	1.7	—
Pea meal.....	—	—	12.0
Ammonium nitrate.....	40.9	40.9	26.5
Common salt.....	9.4	8.0	25.0
Sal ammoniac.....	—	6.0	—
Sodium oxalate.....	12.0	7.4	—

TABLE 58

Composition of the Gelatine-Dahmenites

	GELATINE-DAHMENT	
	A	B
	per cent	per cent
Dinitrolycerine.....	27.4	27.4
Collodion cotton.....	0.6	0.6
Nitrotoluenes.....	4.5	3.5
Naphthaline.....	0.5	—
Ammonium nitrate.....	32.0	32.0
Potassium nitrate.....	2.0	2.0
Sodium nitrate.....	5.5	4.5
Alkali chloride.....	27.5	30.0
Expansion.....	233.0 cc.	205.0 cc.
Charge limit (fire damp).....	350.0 grams	700.0 grams
Charge limit (coal dust).....	700.0 grams	700.0 grams

been tested separately in fire damp and in coal dust in 1908, and had the compositions⁵¹ shown in table 58.

⁵⁰ Kast, *Spreng- und Zündstoffe*, p. 312.

⁵¹ Kast, *Loc. cit.*

Gelatine-Leonit had a gelatinous base of a mixture of trinitro-glycerine and dinitro-glycerine, and was in general of a composition similar to that of Gelatine-Dahmenit. Both types have proved very good. However they were more expensive than the corresponding nitro-glycerine explosives and aside from their non-freezing properties they offered no special advantages so that their manufacture was given up after a few years.

A French so-called gelatinous permissible explosive based upon dinitro-glycerine of the composition:⁴¹

	per cent
Dinitro-glycerine	35.0
Nitro-cellulose	0.7
Ammonium nitrate	38.4
Tetra-nitrotole	2.5
Cellulose	2.0
Sodium oxalate	12.0
Ammonium chloride	9.4

is not a permissible when tested according to the German test.

There should also be mentioned the low freezing permissible explosives still permitted in France and called "Grisouttes" and dinitro-glycerine of which Grisoutine G has the following composition:⁴²

	per cent
Nitro-glycerine	23.3
Dinitro-glycerine	5.8
Nitro-cellulose	0.9
Ammonium nitrate	70.0

Nothing is known regarding practical introduction of these two explosives.

⁴¹ Kast p. 317, and Dautriche *Mém. poudre salp.* 6, p. 186 (1911-12).

⁴² Kast p. 318, and Dautriche *Mém. poudre salp.* 16, p. 72 (1911-12).

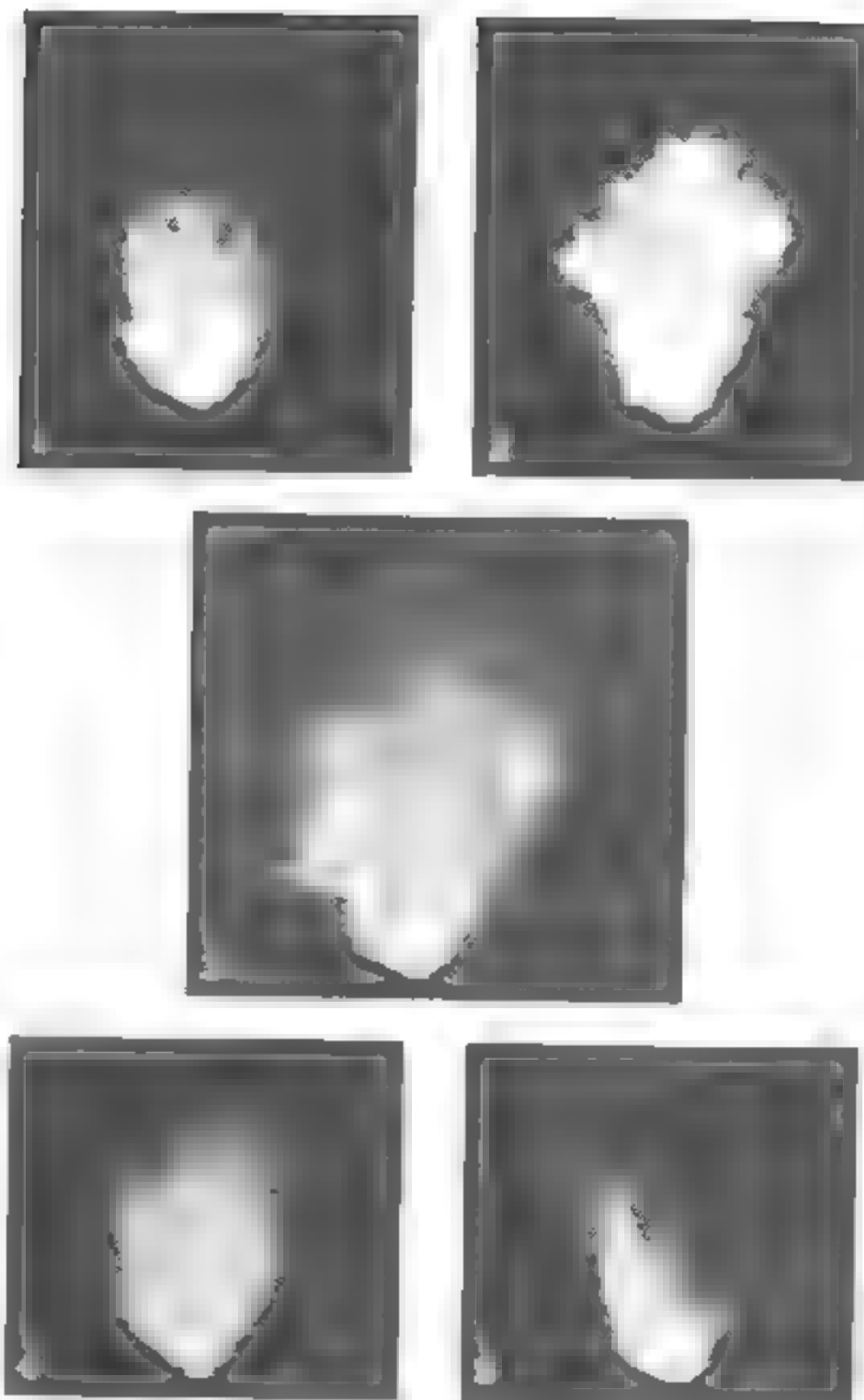


FIGURE 1

1. LABORATORY FRAMES FOR TESTING CERTAIN EXPLOSIVES.
 The top two frames show the results of tests on a mixture of 30 percent
 of nitro-glycerine and 70 percent of ammonium nitrate. The middle frame
 shows the result of a test on a mixture of 30 percent of nitro-glycerine
 and 70 percent of ammonium nitrate. The bottom two frames show the
 results of tests on a mixture of 30 percent of nitro-glycerine and 70 percent
 of ammonium nitrate.

1. Explosives for Rock Work. b. Ammonium nitrate explosives. 6, Ammonit 1 (Astralit). 7, Ammonit 2 (Astralit o.N.) 8, Ammonit 3 (Astralit V). 9, Ammonit 4 (Astralit V o.N.). 10, Ammonal (Ammonit 5).

PHOTOGRAPHS OF FLAMES OF EXPLOSION OF CERTAIN EXPLOSIVES

PLATE II

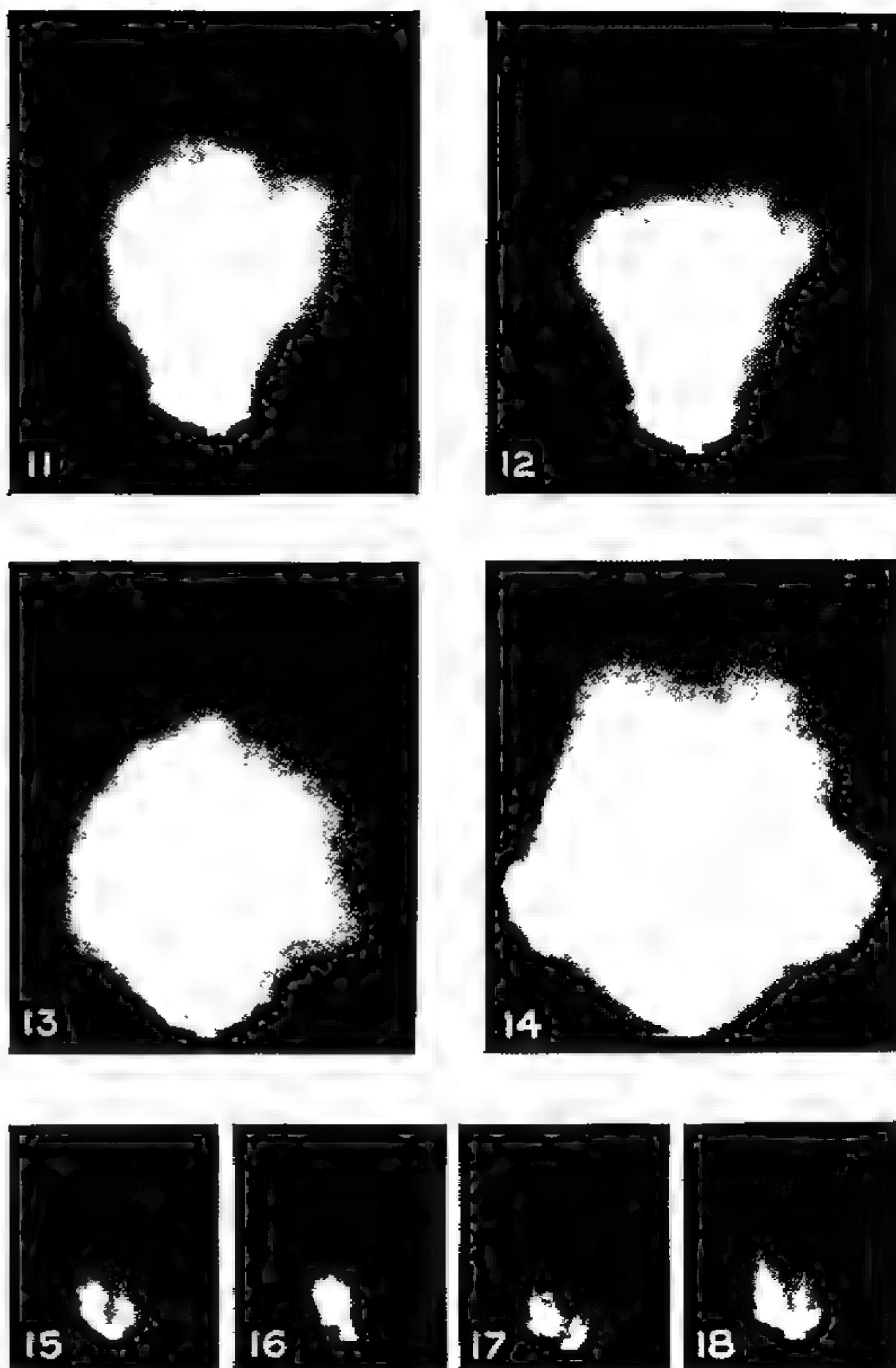
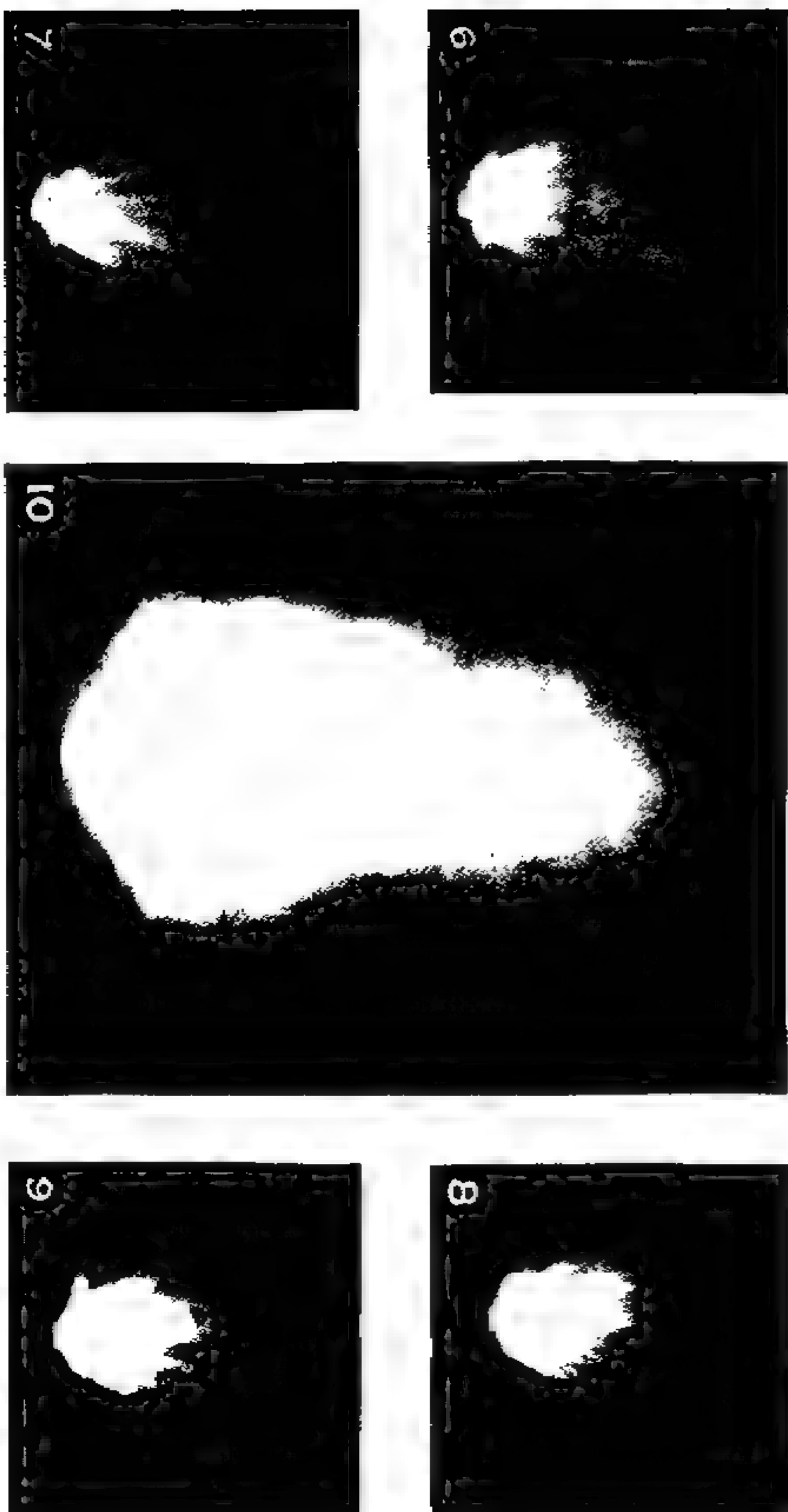


PLATE III

PHOTOGRAPHS OF FLAMES OF EXPLOSION OF CERTAIN EXPLOSIVES

I. Explosives for Rock Work. c. Chlorate explosives. 11, Chloratit 1 (Gesteins-Koronit). 12, Chloratit 2 (Gesteins-Koronit o.N.).

d. Perchlorate explosives. 13, Perchloratit 1 (Perkoronit a). 14, Perchloratit 2 (Perkoronit b).

II. Explosives safe in gaseous and dusty mines. (Permissible explosives.) 15, Wetter-Delonit A. 16, Wetter-Astralit A. 17, Wetter-Nobelit A. 18, Nobelit 20.

CHAPTER XXIV

EXPLOSIVES WITH A LOW NITROGLYCERINE CONTENT

In the last few decades nitroglycerine has attained no little importance as an addition in small quantities to powdery explosives which are compounded with oxidizing salts as a basis. Besides certain chlorate and perchlorate explosives, the main representatives of this class are the safety ammonium nitrate explosives, which play an important part in stone quarries, potash and rock salt mines, as well as in agriculture, e.g., in stump blasting. The ammonium nitrate explosives with a low nitroglycerine content, which are both safe to handle and permissible in fire damp and coal dust, are of no less importance in coal mining.

The value of this small addition of nitroglycerine consists in ensuring detonation and propagation in the explosive in question, a very important factor with the weak permissible explosives. Furthermore, their plasticity, density, velocity of detonation and brisance is thereby somewhat improved, while on the other hand their safety in handling is not affected unfavorably, provided that the addition of nitroglycerine does not exceed 5 per cent.

Often some collodion cotton, as a rule about 0.1 per cent, is also added to the explosive, with the idea of holding the nitroglycerine in the explosive more firmly and preventing any possible exudation. In actual practice this precaution has been found to be unnecessary, since the finely divided nitroglycerine does not exude from the explosive even when the latter becomes moist. Moreover it has not been shown that with the separate addition of collodion cotton and nitroglycerine in such an extreme dilution gelatinization takes place. It is doubtful if the small quantity of collodion cotton can be sufficiently finely divided in manufacturing operations as to come uniformly into contact with the nitroglycerine everywhere. With such explosives the nitroglycerine is always added in the liquid form, and the explosive used for comparison by the German Railway Commission is an ammonium nitrate explosive containing no collodion cotton, the well-known Donarit of the E. V. O.

The nitroglycerine permeates the pulverent explosive in a liquid condition and in a very finely divided state, "moistens" it somewhat, and while in this form it retains its sensitiveness to an initial impulse

and imparts this property to the whole mass, unless other desensitizing substances which hinder the passage of the explosive wave prevent such action. This can occur with too large additions of desensitizing oils, such as paraffine oil, or liquid or plastic, low-nitrated, insensitive nitrocompounds which destroy the pulverent state of the mixture and render it too moist and dense. The latter compounds also dissolve in nitroglycerine and change its physical properties, i.e. desensitize it.

On the contrary, the high-nitrated nitrocompounds such as trinitrotoluene or dinitrotoluene, desensitize only slightly, although they dissolve in nitroglycerine to a certain extent.¹

On the other hand, the nitroglycerine is present in these explosives in such a state of dilution that their character is not appreciably changed either as regards chemical stability or behavior on heating, igniting or to mechanical effects such as shock and friction.

Kast² states that small additions of nitroglycerine increase the sensitiveness of ammonium nitrate explosives to shock. However, this is not generally the case, but other properties of the explosive also play an important part, such as a more powdery or a softer plastic condition. Also the quantity and nature of the nitrocompounds used are not without influence.

The safety ammonium nitrate explosives allowed in unrestricted freight traffic by the German Railway Commission almost all contain 4 per cent nitroglycerine, or only in exceptional cases 5 per cent.³ Donarit, containing 80 per cent ammonium nitrate, 12 per cent trinitrotoluene, 4 per cent rye flour and 4 per cent nitroglycerine is used for comparison.

A number of chlorate and perchlorate explosives are allowed limited transportation on the German Railways (Group 2 Explosives), such as the Gesteins-koronites, Albites, Perchlorites and Perkoronites, used mainly during the World War, and as a rule containing 4 per cent nitroglycerine. Cheddit, containing no nitroglycerine, was used for comparison.

¹ See Solubility of Nitrocompounds in Nitroglycerine, Part I.

² Kast, *Spreng- und Zündstoffe*, 5, Ammonium Nitrate Explosives, p. 321.

³ See Supplement C of the Railway Regulations I, Ia, Explosives. A. Blasting Explosives, Group 1.

EXPLOSIVES FOR USE IN ROCK, WITH OXIDIZING SALTS AS THE BASIS, AND CONTAINING SMALL QUANTITIES OF NITROGLYCERINE

Ammonium nitrate explosives

The oldest ammonium nitrate explosives, such as Roburit and the Favier explosives used in Belgium, as well as the French ammonium nitrate explosives Grisou-Naphtalite-roche, Grisoutolite-roche and others, contain no nitroglycerine. They consist of ammonium nitrate, often with some potassium nitrate and dinitronaphthalene, trinitronaphthalene or trinitrotoluene. Their disadvantage in using insensitive explosive nitrocompounds, such as the naphthalene derivatives, is low sensitiveness and defective propagation.

TABLE 59

Composition of the first ammonium nitrate explosives containing a small amount of nitroglycerine

	DONARIT	DONARIT I	ASTRALIT	ASTRALIT IA
	per cent	per cent	per cent	per cent
Ammonium nitrate.....	80	67	80	68.3
Trinitrotoluene.....	12	25	12	25.0
Vegetable meals.....	4	4	3	2.7
Charcoal.....	—	—	1	—
Nitroglycerine.....	4	4	4	4.0

The first ammonium nitrate explosives with a small addition of nitroglycerine were Donarit and Astralit of the Sprengstoff-A.-G. Carbonit and the Dynamit A.-G. vomals A. Nobel & Co. Gesteins-Westfalit of a similar composition was brought out by the Westfälisch-Anhaltische Sprengstoff-A.-G.

The oldest representatives of these had the composition shown in table 59. These explosives gave a lead block expansion of 380 to 400 cc. net, and velocities of detonation of over 4000 meters per second. The types designated as I and Ia were also called reinforced Donarit and Astralit. Their higher trinitrotoluene content gave them a higher density, velocity of detonation and brisance. Gesteins-Westfalit I contained 73.5 per cent ammonium nitrate, 6 per cent potassium nitrate, 7.5 per cent trinitrotoluene, 5 per cent dinitrotoluene, 5 per cent meal and 3 per cent nitroglycerine.

Supplement C of the German Railway Regulations contains a number of explosives of similar composition, such as Ammonfördit, Dominit, Lignosit, Prosperit, Rhenanit, Gesteins-Romperit, Gesteins Siegenit, etc.

After the Prussian Police Regulation of January 25, 1923, on the sale of explosives to mines had come into effect, all these phantastic names of the various plants for the same category of explosives for Prussian mining went into the discard, and the designations were simplified for all explosives for use in rock.

Only ammonium nitrate explosives according to the following definition, which made possible a gradation of strength, were then sold to Prussian mines under the designation "Ammonit" as ammonium nitrate explosives for rock work. It is expected that this movement toward simplification of explosives will spread to other fields and extend in time to operations not under the supervision of the Chief Mining Council, such as stone quarries, and finally be adopted by the other German states,

Ammonit 1

	per cent
Ammonium nitrate, of which up to 10 per cent of the total explosive may be replaced by potassium nitrate.....	77-85
Vegetable meal and/ or solid hydrocarbon.....	1- 6
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine.....	10-18
Nitroglycerine (also gelatinized).....	3- 4

Ammonit 2

	per cent
Ammonium nitrate, of which up to 10 per cent of the total explosive may be replaced by potassium nitrate.....	77-87
Vegetable meal and/ or solid hydrocarbon and/ or natural cellulose altered chemically or biologically.....	1- 6
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine, of which up to 4 per cent of the total explosive may be replaced by nitrocellulose.....	12-20

Ammonit 3

	per cent
Ammonium nitrate, of which up to 10 per cent of the total explosive may be replaced by potassium nitrate.....	72-76
Potassium perchlorate.....	3- 5
Vegetable meals and/ or solid hydrocarbon.....	1- 4
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine	11-15
Nitroglycerine (also gelatinized).....	3- 4

Ammonit 4

	per cent
Ammonium nitrate.....	70-77
Potassium perchlorate.....	5-10
Vegetable meals and/ or solid hydrocarbon and/ or natural cellulose altered chemically or biologically.....	1- 4
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine, of which up to 4 per cent of the total explosive may be replaced by nitrocellulose.....	10-16

Ammonit 5

	per cent
Ammonium nitrate, of which up to 5 per cent of the total explosive may be replaced by potassium nitrate.....	73-84
Aluminium.....	2-12
Nitroderivatives of toluene.....	5-15
Potassium perchlorate.....	0- 5
Vegetable meals and/ or cellulose or natural wood pulp altered chemically or biologically.....	0- 4
Solid or liquid hydrocarbon.....	0- 4

Ammonit 6

	per cent
Ammonium nitrate, of which up to 10 per cent of the total explosive may be replaced by potassium nitrate.....	82-88
Vegetable meals and/ or solid hydrocarbon.....	1- 6
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine.....	3- 8
Nitroglycerine (also gelatinized).....	3- 4

Ammonit 7

	per cent
Ammonium nitrate, of which up to 10 per cent of the total explosive may be replaced by potassium nitrate.....	83-88
Vegetable meals and/ or solid hydrocarbon and/ or cellulose or natural wood pulp altered chemically or biologically.....	1- 6
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine, of which up to 4 per cent of the total explosive may be replaced by nitrocellulose.....	7-11

Of these Ammonites 1, 3, and 6 accordingly contain an addition of nitroglycerine, whereas the others are nitroglycerine-free. Ammonites 3 to 5, which also contain potassium perchlorate and aluminum rendered possible the utilization of quantities of Perdit and Ammonal, which contained potassium perchlorate and aluminium, left in the possession of the army at the end of the war. However, the explosives

in question must contain at least 50 per cent of fresh materials according to Section 13 of the above Regulation.⁴

The explosive data of such explosives with and without nitroglycerine, with the explosive Astralit as an example, show the comparison shown in table 60. The strength of such explosives, both with and without nitroglycerine, thus does not differ appreciably when large quantities of high-nitrated nitrocompounds such as trinitrotoluene are used. However, those containing nitroglycerine are

TABLE 60
Composition of the Ammonites

COMPOSITION	ASTRALIT (AMMONIT 1)	ASTRALIT O. N. (AMMONIT 2)
	<i>per cent</i>	<i>per cent</i>
Ammonium nitrate.....	79	80
Trinitrotoluene }.....	17	20
Dinitrotoluene }.....		
Vegetable meal }.....	4	—
Nitroglycerine.....		
Oxygen balance.....	+2.5%	+0.3%
Lead block expansion.....	390.0 cc.	375.0 cc.
Lead block crushing.....	16.2 mm.	16.0 mm.
Sensitiveness.....	No. 1 Cap	No. 3 Cap
Propagation in 30 mm. cartridges.....	12.0 cm.	8.0 cm.
Velocity of detonation.....	5400.0 m/s*	4900.0 m/s*
Density of cartridges.....	1.09	1.03
Heat of explosion.....	957.0 Cal.	1006.0 Cal.
Temperature of explosion.....	2170 °C.	2220 °C.

* When enclosed in steel tubes.

always easier to work and have less tendency to form dust. The small quantity of nitroglycerine is always added to the finished explosive in a fine stream while in the mixing machine, located in a barri-

⁴ These explosives were formerly sold under the names Astralit V, Donarit V, Rivalit P, Rhenanit V, etc., with or without nitroglycerine but with a potassium perchlorate content when using Perdit, and as Donarit A, Astralit A, Rivalit A, Rhenanit A, Romperit A, etc., with aluminium but without nitroglycerine and without perchlorate when using Ammonal. See Supplement C, of the E. V. O., Blasting Explosives, Group 1.

caded building, and mixed 10 to 15 minutes to secure an absolutely homogeneous distribution.⁵

There should be mentioned in this connection the ammonium nitrate explosive with a low nitroglycerine content, called "Monobel," an explosive first made in England and later in the United States as well in considerable quantities. The principle varieties are given in table 61.

Monobels II and III are regarded as permissible in the United States.⁶ Monobel I is permitted in England as an explosive for use in rock. Their properties, and the reasons why they are not made in Germany, have been already described in Chapter XIX under Dynamites with Active Absorbents.

TABLE 61
Composition of Monobels

	MONOBL		
	I	II	III
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Nitroglycerine.....	10	10	10
Ammonium nitrate.....	80	70	70
Common salt.....	—	10	10
Rye flour.....	2	2	—
Wood pulp.....	8	■	—
Fine sawdust.....	—	—	10

Chlorate and perchlorate explosives

While the chlorate explosives formerly used in Germany, such as Cheddite and Silesia explosives, contained no nitroglycerine, during

⁵ For further details regarding the manufacture of ammonium nitrate explosives see Escales, *Die Ammonsalpetersprengstoffe*, and Kast, *Spreng- und Zündstoffe*, p. 317.

⁶ Monobel I is also a permissible in the United States. A very large number of similar nitrate of ammonia permissible explosives are made and used in the United States, all having 10 per cent nitroglycerine or recently nitropolyglycerine. Practically speaking, they are the only permissible explosives used in coal mines in the United States, and the quantity consumed is enormous. In the last few years the tendency has been to reduce the density and so increase the number of cartridges per unit weight. This has proved more economical from the viewpoint of the mine owner. —TRANSLATOR.

the war the manufacture of these explosives received a great impetus on account of the lack of nitrogen compounds, and additions of 4 per cent nitroglycerine were made to them without appreciably altering the characteristic properties of these mixtures and their limited degree of safety in handling.

Group 2 of the Blasting Explosives in Supplement C of the German Railway Regulations includes a number of such explosives which are permitted as freight in limited quantities, 200 kg. The best known of these are the Gesteinskoronites, Albites, Kohlenkoronites, Wet-

TABLE 62

Explosive characteristics of the new, comparatively highly brisant chlorate explosives

	GESTEINS-KORONIT T1	GESTEINS-KORONIT T2
	per cent	per cent
Sodium chlorate.....	72.0	75.0
Vegetable meals.....	1.0-2.0	1.0-2.0
Tri- and Dinitrotoluene.....	20.0	20.0
Paraffine.....	3.0-4.0	3.0-4.0
Nitroglycerine.....	3.0-4.0	—
Oxygen balance.....	+3.0%	+1.9%
Lead block expansion.....	290.0 cc.	280.0 cc.
Lead block crushing.....	20.0 mm.	19.5 mm.
Sensitiveness.....	No. 3 Cap	No. 1 Cap
Propagation in 25 mm. cartridges.....	8.0 cm.	8.0 cm.
Velocity of detonation.....	5000.0 m/s	4300.0 m/s
Density of cartridge.....	1.57	1.46
Heat of explosion.....	1219.0 Cal.	1241.0 Cal.
Temperature of explosion.....	3265°C.	3300°C.

teralbites and Kohlenalbites, the latter having been used as a permissible in coal mines for a short time, but on account of their possible large flame on explosion were soon replaced by ammonium nitrate explosives.

In addition to potassium or sodium chlorate they contain vegetable meals, nitrocompounds such as nitronaphthaline, dinitrotoluene and trinitrotoluene, and hydrocarbons such as naphthaline or paraffine. The nitroglycerine added serves to improve the propagation and raise the brisance.

Up until recently the Gesteins-Koronit T of the Dynamit A.-G. found considerable use in potash mines, stone quarries and iron ore mines, but in the years after the war it has been replaced more and more by the low-percentage dynamites and the perchlorate explosives such as Perkoronit.

The explosive characteristics of the new, comparatively highly brisant chlorate explosives, with and without nitroglycerine, are as given in table 62. The brisance of the explosive containing nitroglycerine is thus greater than the one without. It is remarkable that the latter detonates with the weak No. 1 cap, which is due to its dry, pulverent nature, while the more plastic and softer explosive containing nitroglycerine is somewhat less sensitive and requires a stronger cap.

Likewise the plastic mixture containing nitroglycerine is somewhat less sensitive to shock and friction, in spite of the nitroglycerine present, than the drier explosive with no nitroglycerine.

The above-mentioned Police Regulation provides on the list of mining explosives among those for use in rock in Prussian mining for the following types of chlorate explosives, of which only the first contains nitroglycerine:

Chloratit 1

	per cent
Potassium and/ or sodium chlorate, of which up to 20 per cent of the total explosive may be replaced by potassium perchlorate and/ or potassium nitrate.....	70-80
Nitroderivatives of toluol and/ or naphthaline and/ or diphenylamine.....	12-20
Vegetable meal.....	1- 5
Solid hydrocarbon and/ or oil or fat.....	3- 5
Nitroglycerine (ungelatinized).....	2- 6

Chloratit 2

	per cent
Potassium and/ or sodium chlorate, of which up to 20 per cent of the total explosive may be replaced by potassium perchlorate.....	70-85
Nitroderivatives of toluol and/ or naphthaline and/ or diphenylamine.....	10-20
Vegetable meal.....	1- 5
Solid hydrocarbon and/ or oil and/ or fat.....	3- 5

Chloratit 3

	per cent
Potassium and/ or sodium chlorate.....	88-91
Liquid hydrocarbon with a flash-point not lower than 30°C.....	12- 9

Of the perchlorate explosives the Perchlorites and Wetterperchlorites, as well as Persalites, Gesteins-Persalites and Wetter-Persalites were much used during the war. Here also an addition of 4 per cent, and occasionally 6 per cent nitroglycerine was customary. These explosives were also put on the Railway Regulation List in Group 2 with the chlorate explosives. The Perchlorites contained about 35 per cent potassium perchlorate, about as much ammonium nitrate, and aromatic nitrocompounds, vegetable meals and usually 4 per cent nitroglycerine. The Wetter-Perchlorites contained in addition a corresponding quantity of alkali chloride.

TABLE 63
Composition of the Perkoronites

	PERKORONIT A	PERKORONIT B
	per cent	per cent
Potassium perchlorate.....	58	59
Ammonium nitrate.....	8	10
Tri- and dinitrotoluene, vegetable meal.....	30	31
Nitroglycerine.....	4	—
Oxygen balance.....	+2.2	+1.8
Lead block expansion.....	340.0 cc.	330.0 cc.
Lead block crushing.....	20.0 mm.	18.0 mm.
Sensitiveness.....	No. 3 Cap	No. 3 Cap
Propagation in 25 mm. cartridges.....	6.0 cm.	4.0 cm.
Velocity of detonation.....	5000.0 m/s	4400.0 m/s
Density of cartridge.....	1.58	1.52
Heat of explosion.....	1170.0 Cal.	1160.0 Cal.
Temperature of explosion.....	3145°C.	3115°C.

The Perkoronites had a wide sale in the years after the war, especially in ore mines and stone quarries.⁷ These explosives consist mainly of potassium perchlorate, with a little ammonium nitrate, a large amount of nitrocompounds and some wood meal, with or without nitroglycerine. The recovery of large quantities of potassium perchlorate from the so-called perchlorate mines⁸ of the army stocks was necessary for their manufacture.

⁷ Today their sale has ceased, the stocks of recovered perchlorate being exhausted and fresh perchlorate too high in price.—AUTHOR.

⁸ These mines contained a charge of explosive consisting of potassium perchlorate and nitrocompounds, from which the former could be recovered by leaching out with hot water.

Their action is also highly brisant and about equal to that of the best chlorate explosives. The potassium perchlorate gives off its oxygen less readily than the chlorate and therefore as a basis for explosives it is less sensitive to detonation than the latter. However, dry, powdery perchlorate mixtures are almost as sensitive to shock and friction as the chlorate explosives. On the other hand, good sensitiveness and propagation presupposes the use of high-nitrated nitrocompounds in perchlorate explosives, and here the nitroglycerine addition under certain conditions plays a more important part than in ammonium nitrate explosives.

Two typical examples of these explosives, made by the Dynamit A.-G. and widely used, are shown in table 63, together with their explosive characteristics.

The Prussian Police Regulation of January 25, 1923, regarding the simplification of explosives shows on the list of mining explosives under explosives for rock work the following types of perchlorate explosives under the name of "Perchloratites:"

Perchloratit 1

	per cent
Potassium perchlorate, of which up to 10 per cent of the total explosive may be replaced by ammonium nitrate and/ or potassium nitrate.....	60-75
Vegetable meals.....	1- 5
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine.....	20-30
Nitroglycerine (ungelatinized).....	3- 6

Perchloratit 2

	per cent
Potassium perchlorate, of which up to 10 per cent of the total explosive may be replaced by ammonium nitrate and/ or potassium nitrate.....	62-75
Vegetable meal and/ or solid hydrocarbon.....	1- 8
Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine, of which up to 4 per cent of the total explosive may be replaced by nitrocellulose.....	20-30

Perchloratit 3

	per cent
Potassium and/ or ammonium perchlorate.....	30-40
Ammonium nitrate, of which an equivalent quantity must be replaced by potassium nitrate when ammonium perchlorate is present.....	35-45

Nitroderivatives of toluene and/ or naphthaline and/ or diphenylamine, of which up to 4 per cent of the total explosive may be replaced by nitrocellulose.....	15-20
Vegetable meal and/ or solid hydrocarbon.....	3- 8

PERMISSIBLE EXPLOSIVES HAVING A LOW NITROGLYCERINE CONTENT

Permissible ammonium nitrate explosives with 4 per cent nitroglycerine

Permissible chlorate and perchlorate explosives with low nitroglycerine contents have been described briefly under "Gesteins-sprengstoffe." Since they were mainly used during the war in Germany and attained no great importance they need no further description.

On the other hand the permissible ammonium nitrate explosives, which almost exclusively took care of coal mining during the war years when nitroglycerine was reserved for military purposes, and which even today are used mainly in getting out coal, are of the greatest importance, the gelatinous permissibles similar to dynamite being used for work in the accompanying rock.

The present severe test conditions for permissible explosives have led to a great diminution of brisance as compared to the older representatives, which fact at the same time gives a particular importance to ensuring sensitiveness and propagation.

In Germany this is accomplished by the addition of nitroglycerine, which in Prussia is made obligatory to the extent of 4 per cent by Section 16 of the Police Regulations of January 25, 1923, while in other countries, as in France, less value is apparently placed upon this factor. For example, France permits for work in coal beds, in addition to ammonium nitrate explosives containing nitroglycerine, *Grisou-Dynamite-couche*, containing:

	per cent	per cent
Nitroglycerine.....	12.0	12.0
Collodion cotton.....	0.5	0.5
Ammonium nitrate.....	87.5	82.5
Potassium nitrate.....	—	5.0

also the nitroglycerine-free ammonium nitrate explosive called "*Grisou-Naphtalite-couche*" containing:

	per cent	per cent
Trinitronaphtaline.....	5.0	5.0
Ammonium nitrate.....	95.0	90.0
Potassium nitrate.....	—	5.0

and "*Grisoutolite-couche*" containing:

	per cent
Trinitrotoluene.....	6.5
Potassium nitrate.....	5.0
Ammonium nitrate.....	88.5

Since even a slight absorption of moisture can affect the sensitiveness of such mixtures considerably, and in view of the great hygroscopicity of ammonium nitrate they are not regarded as permissible under German conditions.

The same thing applies, for example, to the French permissible explosive for accompanying rock work, called "*Grisou-Naphtalite-roche*," which has the following composition:

	per cent	per cent
Dinitronaphtaline.....	8.5	8.5
Ammonium nitrate.....	91.5	86.5
Potassium nitrate.....	—	5.0

The English Permitted List contains a number of nitroglycerine-free permissible ammonium nitrate explosives,⁹ but according to reports permissible explosives containing nitroglycerine are used almost exclusively.

The permissible ammonium nitrate explosives can be divided into two main classes, namely, those in which the average ammonium nitrate content of about 55 to 75 per cent has an available oxygen wholly or mostly used to oxidize the carbonaceous ingredients such as nitrocompounds and meal, and in which the heat of explosion and brisance are reduced by certain materials such as chlorides, and those having a high ammonium nitrate content of 75 to 80 per cent or more, whose low heat of explosion and brisance depend upon a very incomplete utilization of the oxygen of the ammonium nitrate in the presence of very small contents of carbonaceous ingredients. The latter type enjoy the greatest popularity today and are the most widely manufactured.

To the first class belong the older *Wetter-Astralites*, *Ammon-Nobelites*, *Ammon-Carbonites*, *Kohlen-Westfalites*, *Detonites*, *Prosperites* and the new *Wetter-Lignosites* and *Wetter-Ammoncahü-cites*. Examples are given in table 64. Of these explosives the

⁹ Kast, *Spreng- und Zündstoffe*, p. 339.

Detonit V was used especially as a war explosive, since it required the release of no aromatic nitrocompounds. During that period it was used largely in getting out coal. Two English permissible explosives which belong to the same class¹⁰ are given in table 65.

TABLE 64
Composition of explosives with a low ammonium nitrate content

	AMMON- NOBELIT A	AMMON- CARBONIT II	DETONIT V	PROSPERIT V
	per cent	per cent	per cent	per cent
Ammonium nitrate.....	61.0	56.4	66.0	60.0
Sodium nitrate.....	3.0	7.0	—	5.0
Meal.....	7.5	4.0	2.0	4.0
Glycerine.....	3.0	5.0	—	—
Powdered coal.....	—	—	4.0	—
Nitrotoluenes.....	1.0	—	—	6.0
Alkali chloride.....	20.5	22.6	22.0	21.0
Nitroglycerine.....	4.0	5.0	4.0	4.0
Oxygen balance.....	±0.0	-10.0	-4.8	+2.7
Expansion.....	215.0 cc.	210.0 cc.	220.0 cc.	235.0 cc.

TABLE 65
Composition of two English permissible explosives

	SUPER- EXCELLITR 2	MELLING POWDER
	per cent	per cent
Ammonium nitrate.....	48.0-51.0	51.0-55.0
Potassium nitrate.....	19.0-21.0	—
Sodium nitrate.....	—	11.0-13.0
Ammonium oxalate.....	14.0-16.0	18.0-20.0
Ammonium chloride.....	4.0- 6.0	—
Wood meal.....	—	3.0- 5.0
Trinitrotoluene.....	—	5.0- 7.0
Nitroglycerine.....	4.0- 6.0	4.0- 6.0
Moisture.....	1.5	2*

* The moisture is the water of crystallization of the ammonium oxalate.

A large number of ammonium nitrate explosives with a high ammonium nitrate content and 4 per cent nitroglycerine have be-

¹⁰ Kast, *Spreng- und Zündstoffe*, p. 338-9.

come known. Ammoncarbonit is the oldest representative of this class, and has the composition: 82 per cent ammonium nitrate, 10

TABLE 66
Composition of explosives with a high ammonium nitrate content

	AMMON- NOBELIT	KOHLN- WESTFALIT I	KOHLN- WESTFALIT IV
	per cent	per cent	per cent
Ammonium nitrate.....	78.0	83.0	73.0
Potassium nitrate.....	5.0	7.0	2.8
Barium nitrate.....	—	2.0	—
Alkali chloride.....	8.0	—	15.0
Meal.....	5.0	2.0	1.0
Trinitrotoluene.....	—	2.0	—
Dinitrotoluene.....	—	—	5.0
Nitroglycerine.....	4.0	4.0	3.2
Oxygen balance.....	+11.8	+16.4	+8.8
Expansion.....	200.0 cc.	230.0 cc.	200.0 cc.

TABLE 67
Explosives used during and after the World War

	DETONIT VI OR 14A	DETONIT XIV	KOHLN- WESTFALIT V
	per cent	per cent	per cent
Ammonium nitrate.....	82.0	82.0	83.0
Potassium nitrate.....	—	10.0	8.0
Barium nitrate.....	—	—	2.0
Common salt.....	10.5	—	—
Wood meal.....	2.0	1.5	1.5*
Powdered coal.....	0.5	—	—
Montan wax.....	—	—	1.5
Nitronaphthaline.....	1.0	2.5	—
Nitroglycerine.....	4.0	4.0	4.0
Oxygen balance.....	+10.9	+13.6	+13.5
Expansion.....	230.0 cc.	235.0 cc.	230.0 cc.

* Potato meal.

per cent potassium nitrate, 4 per cent meal, 3.8 per cent nitroglycerine and 0.2 per cent collodion cotton. It has a lead block expansion of about 200 cc., a velocity of detonation of 3100 m/s., a heat of explo-

TABLE 68
Permissible ammonium nitrate explosives in Prussian mining since
January 1, 1924

NUMBER	NAME	CHEMICAL COMPOSITION	COMPANY AND PLANT	MAXIMUM CHARGE	
				In gas	In coal dust
1	Wetter-Detonit A	<i>per cent</i> 82.00 NH_4NO_3 1.00 N. naphthaline 2.00 Wood meal 0.50 Coal powder 4.00 Gelatinized nitroglycerine	1. Dyn. A.-G. vorm. Alfred Nobel & Co., Hamburg, Schlebusch Plant	800	800
		10.50 KCl 100.00	2. Westdeutsche Sprengstoff A.-G. Dortmund, Rummenohl Plant	800	800
			3. Deutsche Sprengstoff-A.-G. Hamburg, Wahn Plant	800	800
2	Wetter-Detonit B	81.00 NH_4NO_3 8.00 $\text{Ba}(\text{NO}_3)_2$ 2.00 Trinitrotoluene 1.00 Wood meal 4.00 Nitroglycerine 4.00 KCl 100.00	1. Dynamit A.-G. vorm. Alfred Nobel & Co. Hamburg, Schlebusch Plant	800	800
			2. Carbonit A.-G. Hamburg, Schlebusch Plant	800	800
3	Wetter-Donarit A	82.00 NH_4NO_3 1.00 Nitronaphthaline 2.00 Wood meal 0.50 Coal powder 4.00 Gelatinized nitroglycerine 10.50 KCl 100.00	Carbonit A.-G. Hamburg, Schlebusch Plant	800	800
4	Wetter-Donarit B	81.00 NH_4NO_3 8.00 $\text{Ba}(\text{NO}_3)_2$ 2.00 Trinitrotoluene 1.00 Wood meal 4.00 Nitroglycerine 4.00 KCl 100.00	Same	800	800

TABLE 68—Continued

NUMBER	NAME	CHEMICAL COMPOSITION	COMPANY AND PLANT	MAXIMUM CHARGE	
				In gas	In coal dust
5	Wetter-Fördit A	<i>per cent</i> 75.00 NH_4NO_3 2.00 Wood meal 0.75 Coal 4.00 Nitroglycerine 18.25 KCl 100.00	Aktiengesellschaft Siegener Dynamit-Fabrik, Köln, Förde Plant	800	800
6	Wetter-Dahmenit A	81.00 NH_4NO_3 8.00 $\text{Ba}(\text{NO}_3)_2$ 2.00 Trinitrotoluene 1.00 Wood meal 4.00 Nitroglycerine 4.00 KCl 100.00	Westdeutsche Sprengstoffwerke A.-G., Dortmund; Rummenohl Plant	800	800
7	Wetter-Sonnit A	81.00 NH_4NO_3 8.00 $\text{Ba}(\text{NO}_3)_2$ 2.00 Trinitrotoluene 1.00 Wood meal 4.00 Nitroglycerine 4.00 KCl 100.00	Deutsche Sprengstoff A.-G., Hamburg, Wahn Plant	800	800
8	Wetter-Westfalit A	84.00 NH_4NO_3 2.40 $\text{Ba}(\text{NO}_3)_2$ 1.60 Naphthaline 4.00 Nitroglycerine 8.00 KCl 100.00	Westfälisch-Anhaltische Sprengstoff-A.-G., Berlin, a) Sythen Plant, b) Reinsdorf Plant	800	800
9	Wetter-Westfalit B	82.00 NH_4NO_3 1.50 Wood meal 1.50 Coal 4.00 Nitroglycerine 11.00 KCl 100.00	Same	800	800
10	Wetter-Westfalit C	80.00 NH_4NO_3 4.00 KNO_3 2.00 $\text{Ba}(\text{NO}_3)_2$ 2.00 Wood meal	Same	800	800

TABLE 68—*Concluded*

NUMBER	NAME	CHEMICAL COMPOSITION	COMPANY AND PLANT	MAXIMUM CHARGE	
				In gas	In coal dust
		per cent		grams	grams
10	Wetter-Westfalit C	3.00 Desensitized trinitrotoluene 4.00 Nitroglycerine 5.00 KCl 100.00			
11	Wetter-Lignosit A	62.00 NH_4NO_3 5.00 KNO_3 6.30 Trinitrotoluene 0.70 Dinitrotoluene 4.00 Wood meal 4.00 Nitroglycerine 18.00 Common salt 100.00	1. Aktien-Gesellschaft Lignose, Berlin, Kruppamühle Plant. 2. Westlignose A.-G. Berlin, Nüssau Plant	800	800
12	Wetter-Lignosit B	61.50 NH_4NO_3 3.00 $\text{Ba}(\text{NO}_3)_2$ 5.00 Dinitrotoluene 4.00 Wood meal 4.00 Gelatinized nitroglycerine 22.50 Common salt 100.00	Westlignose A.-G. Berlin, Nüssau Plant	800	800
13	Wetter-Ammoncahücit A	64.70 NH_4NO_3 8.0 Trinitrotoluene 2.00 Coal 1.30 Wood meal 4.00 Gelatinized nitroglycerine 20.00 Common salt 100.00	Deutsche Cahücitwerke A.-G., Gnaschwitz, Gnaschwitz Plant	800	800
14	Wetter-Ammoncahücit B	67.00 NH_4NO_3 6.00 Dinitrotoluene 1.50 Wood meal 1.50 Coal 4.00 Gelatinized nitroglycerine 20.00 Common salt 100.00	1. Deutsche Cahücitwerke A.-G., Gnaschwitz, Gnaschwitz Plant	700	800

TABLE 69

Explosive characteristics of ammonium nitrate explosives

	WETTER-DETONIT A WETTER-DONARIT A	WETTER-DETONIT B WETTER-DONARIT B WETTER-DAHMENIT A WETTER-SONNIT A
Oxygen balance.....	+10.9%	+16.1%
Lead block expansion.....	230.0 cc.	220.0 cc.
Lead block crushing.....	8.5 mm.	8.3 mm.
Sensitiveness.....	No. 3 Cap	No. 3 Cap
Propagation in 30 mm. cartridges.....	4.0 cm.	4.0 cm.
Velocity of detonation.....	3600.0 m/s	3650.0 m/s
Density of cartridge.....	1.04	1.06
Heat of explosion.....	548.0 Cal.	462.0 Cal.
Temperature of explosion.....	1520°C.	1388 °C.
Safety in fire damp*.....	600.0 grams	550.0 grams
Safety in coal dust*.....	600.0 grams	500.0 grams

* According to results at the Derne Testing Station.

TABLE 70

French, Belgian and English explosives

	GRISOUTINE A	GRISOUTINE B
	per cent	per cent
Ammonium nitrate.....	90.45	94.0
Nitroglycerine.....	4.85	5.9
Nitrocellulose.....	0.15	0.1
Rosin	4.55	—

	FLAMMIVORR		FRAC-TORITE	SUPER-EXCELITE	SUPERITE
	I	III			
	per cent	per cent	per cent	per cent	per cent
Ammonium nitrate.....	82.0	72.0	75.0	73.5-77.0	80.0-84.0
Sodium nitrate.....	10.0	—	10.0	—	—
Potassium nitrate.....	—	—	—	6.5-8.0	9.0-11.0
Ammonium oxalate.....	—	—	7.0	9.0-11.0	—
Ammonium chloride.....	—	—	—	—	—
Ammonium sulphate	—	9.0	—	—	—
Barium sulphate.....	—	7.0	—	—	—
Meal.....	4.0	—	4.0	2.0-4.0	—
Dextrine-starch.....	—	6.0	—	—	2.0-5.0
Nitroglycerine.....	4.0	6.0	4.0	3.5-5.0	3.5-4.5

sion of 609 Calories, and a temperature of explosion of 1648°C.¹¹ Ammon-Nobelit and the Kohlenwestfalites I and IV appeared at about the same time.¹²

During, and some years after the World War the explosives shown in table 67 were used to a great extent. It is the custom to wrap these explosives in a double shell and immerse in paraffine. Before using, the external, paraffined shell is removed. They are also tested at the testing station after removal of the external wrapper, and contained in only the usual paper shell. This is because the high oxygen excess of these mixtures takes part in the combustion of the paraffine, and with a simple paraffined shell the temperatures of explosion are raised and the permissibility reduced. This action has actually been observed.

In recent times it has also been shown that explosives like Detonit XIV are not sufficiently safe in coal dust on account of their rather high potassium nitrate content. For this reason the quantity of this substance has been reduced or other salts substituted.

From January 1, 1924, on, there may be used in Prussian mining only the following permissible ammonium nitrate explosives with 4 per cent nitroglycerine which are found on the first list of mining explosives.¹³ Of these the first ten belong to the last-mentioned type with a high ammonium nitrate content and a high oxygen excess, and the last four to the type having a moderate ammonium nitrate content and a large alkali chloride content. (See table 68.)

The explosive characteristics of Wetter-Detonit A and B, Wetter-Donarit A and B, Wetter-Dahmenit A and Wetter-Sonnit A are as shown in table 69. The French permissible explosives Grisoutine A and B, not used at present, belong to this class or type, also the Belgian Flammivore and Fractorite, as well as the English Super Excellite and Superite. (See table 70.)

So-called semi-plastic permissible ammonium nitrate explosives with 10 to 12 per cent nitroglycerine

A new type of permissible ammonium nitrate explosives with a low nitroglycerine content, the so-called semi-plastic or semi-gelatinous

permissibles, appeared about 1910 in the form of the Gelatine-Carbonites, Neu-Nobelites, Kohlen-Salites, etc.

These explosives are in a certain sense ammonium nitrate explosives, but on the other hand cannot be compared with the gelatinous

TABLE 71
Compositions of explosives used before the World War

	NEU-NOBELIT 0	GELATINE- CARBONIT III	KOHLEN- SALIT
	per cent	per cent	per cent
Gelatinized nitroglycerine.....	12.0	10.1	12.5
Glycerine.....	4.0	5.0	—
Meal.....	6.0	4.0	2.5
Nitrocompounds.....	—	—	7.0
Ammonium nitrate.....	50.0	46.4	41.0
Sodium nitrate.....	3.0	7.0	—
Alkali chloride.....	20.0	27.5	37.0
Talc.....	5.0	—	—
Oxygen balance.....	-0.6%	+2.2%	-2.6%
Expansion.....	220.0 cc.	200.0 cc.	190.0 cc.

TABLE 72
Compositions of explosives used during and after the World War

	NEU-NOBELIT	
	XV	XVI
	per cent	per cent
Gelatinized nitroglycerine.....	12.0	12.0
Wood meal and coal.....	4.0	3.0
Nitrocompounds.....	2.0	3.0
Ammonium nitrate.....	54.0	54.0
Alkali chloride.....	28.0	28.0
Oxygen balance.....	+0.6%	+2.9%
Expansion.....	225.0 cc.	225.0 cc.

mixtures. They usually contain 10 to 12 per cent nitroglycerine, which is added as a liquid to the mixed absorbents containing some collodion cotton in the mixer. The process of manufacture is just the same as that of the ammonium nitrate explosives. They have

¹¹ Bichel, *Gluckauf* (1904), p. 1043.

¹² Kast, *Spreng- und Zündstoffe*, p. 332.

¹³ Carl Heymanns Verlag, see also *Deutscher Reichsanzeiger and Preussischer Staatsanzeiger*, 1923, No. 41, Suppl. 2.

TABLE 73

Permissible explosives from the Prussian mining list of January, 1924

NUMBER	NAME	CHEMICAL COMPOSITION	FIRM AND PLANT	MAXIMUM CHARGE	
				In fire damp	In coal dust
		<i>per cent</i>		<i>grams</i>	<i>grams</i>
15	Wetter-Astralit A	12.0 Gelatinized nitro-glycerine 57.0 Ammonium nitrate 2.0 Wood meal 2.0 Coal powder 27.0 Common salt 100.0	Dynamit A.-G. vorm. A. Nobel & Co., Hamburg, Schlebusch Plant	800	800
16	Wetter-Sigrit A	12.0 Gelatinized nitro-glycerine 57.0 Ammonium nitrate 2.0 Wood meal 2.0 Coal powder 27.0 KCl 100.0	A.-G. Siegenger Dynamitfabrik, Köln, Förde Plant	800	800
17	Wetter-Salit A	12.0 Gelatinized nitro-glycerine 55.0 Ammonium nitrate 3.0 Coal 2.0 Wood meal 28.0 KCl 100.0	Westfälisch-Anhaltische sprengstoff-A.-G., Berlin. (a) Sythen Plant, (b) Reinsdorf Plant	700	800
18	Wetter-Bal-durit A	12.0 Gelatinized nitro-glycerine 50.0 Ammonium nitrate 2.0 Dinitrotoluene 2.0 Wood meal 0.5 Coal powder 33.5 Common salt 100.0	Westlignose A.-G., Berlin, Nüssau Plant	600	800
19	Wetter-Bavarit A	12.0 Gelatinized nitro-glycerine 55.0 Ammonium nitrate 3.0 Dinitrotoluene 1.0 Coal 1.0 Wood meal 28.0 Common salt 100.0	1. Bayrische Sprengstoffwerke und Chemische Fabriken A.-G., Nürnberg, Neumarkt Plant 2. Deutsche Cahücitwerke A.-G., Gnaschwitz, Gnaschwitz Plant	800	800

EXPLOSIVES WITH LOW NITROGLYCERINE CONTENT

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TABLE 73—Concluded

NUMBER	NAME	CHEMICAL COMPOSITION	FIRM AND PLANT	MAXIMUM CHARGE	
				In fire damp	In coal dust
		<i>per cent</i>		<i>grams</i>	<i>grams</i>
20	Wetter-Bavarit B	12.0 Gelatinized nitro-glycerine 56.0 Ammonium nitrate 2.0 Trinitrotoluene 2.0 Dinitrotoluene 28.0 Common salt 100.0	1. Bayrische Sprengstoffwerke und Chemische Fabriken A.-G., Gnaschwitz, Neumarkt Plant 2. Deutsche Cahücitwerke A.-G., Gnaschwitz, Gnaschwitz Plant	800	800

the form of a relatively heavy, moist powder, which is cartridgeed with the same machines as guhr dynamite. The nitroglycerine is present in the form of a liquid or slightly gelatinized state, but it has no particular tendency to exude. Paraffined paper is used for the cartridge shells, just as with gelatine dynamite, because the nitroglycerine would soak through ordinary paper. On the other hand, individual dipping of the cartridges in ceresine,¹⁴ as is done with other ammonium nitrate explosives containing 4 per cent nitroglycerine, is not necessary, since the hygroscopic ammonium nitrate is better protected against absorption of moisture by the relatively greater saturation with nitroglycerine than when in the dry, powdery mixtures, and moreover the higher nitroglycerine content makes the sensitiveness higher and propagation more certain. Often the so-called bag packing is used, i.e., two paper bags, each containing 125 kg., are each dipped into paraffin, put into the usual 2.5 kg. carton, and this again dipped.

These explosives are not regarded as safe to handle, and do not enjoy the less severe transportation requirements of the ammonium nitrate explosives containing 4 per cent nitroglycerine.

¹⁴ In many European plants cartridges are dipped in paraffine wax one by one, and allowed to cool. In the United States this is done mechanically. —TRANSLATOR.

They were used in German mines in varying amounts, especially in the period of glycerine scarcity during the war and in the years following. However, for work in accompanying rock the stronger gelatinous permissibles with 25 to 30 per cent nitroglycerine are preferred in view of the small difference in price.

TABLE 74
Explosive characteristics of Prussian permissible explosives

	NEU-NOBELIT XVI	WESTER-ASTRALEIT A
Oxygen balance.....	+2.8%	+4.1%
Lead block expansion.....	225.0 cc.	210.0 cc.
Lead block crushing.....	13.0 mm.	10.0 mm.
Sensitiveness.....	No. 1 Cap	No. 1 Cap
Propagation with 30 mm. cartridges.....	25.0 cm.	25.0 cm.
Velocity of detonation.....	4600.0 m/s	3800.0 m/s
Density of cartridge.....	1.20	1.21
Heat of explosion.....	643.0 Cal.	601.0 Cal.
Temperature of explosion.....	1828°C.	1738°C.
Safety in fire damp*.....	650.0 grams	600.0 grams
Safety in coal dust*.....	700.0 grams	700.0 grams

* Results of tests at the Derne Testing Station.

TABLE 75
English permissible explosives

	SUPER EXCELLITE 1	MONARKITE 2	RDX POWDER	STOMMONAL 3
Nitroglycerine.....	8.5-10.5	9.0-11.0	11.0-13.0	9.0-11.0
Ammonium nitrate.....	62.0-65.0	51.0-54.0	53.0-61.0	59.5-62.5
Sodium nitrate.....	—	5.0-7.0	—	—
Common salt.....	18.5-20.5	21.0-23.0	18.5-20.5	16.0-18.0
Ammonium oxalate.....	—	—	—	5.0-7.0
Wood meal, dried at 100°C.....	4.5-6.5	—	7.0-8.6	5.0-7.0
Cereal meal, dried at 100°C.....	—	6.5-8.5	—	—
Magnesium carbonate.....	0-1.5	0-1.5	—	—
Moisture.....	0-2.0	0-2.0	0-2.5	0-2.0

In France this type is permitted for work in coal seams, and in England also they are used to a great extent in coal. Typical compositions from the period before the war are shown in table 71. The composition given in table 72 was widely used during and after the war.

On the first Prussian Mining List of January 1, 1924, only the six representatives of this type shown in table 73 were allowed in Prussian mining. The explosive characteristics can be seen from the examples in table 74.

In France the following explosives are permitted for work in coal seams under the designation of Grisou-Dynamite-couche:

	per cent	per cent
Nitroglycerine.....	12.0	12.0
Collodion cotton.....	0.5	0.5
Ammonium nitrate.....	87.5	82.5
Potassium nitrate.....	—	5.0

New English representatives of this type which were added to the Permitted List of Explosives in 1920 are shown in table 75.

CHAPTER XXV

NITROGLYCERINE SMOKELESS POWDER AND SEMI-FINISHED SMOKELESS POWDER AS EXPLOSIVES

EXTRACTION OF NITROGLYCERINE POWDER

At the close of the war there were several thousand tons of smokeless powder left on hand, for which the most rapid possible, economical utilization had to be found, or the treaty of peace would have prescribed their destruction.

While pure nitrocellulose powder lends itself to various commercial uses, e.g., the manufacture of lacquers and artificial silk in considerable quantities, such a method of utilization of nitroglycerine powder could not be considered on account of the physical and physiological properties of the nitroglycerine, together with the danger and inconvenience.

Commercial application and utilization of this material, which represented considerable commercial value, proved to be possible in two ways, one through the recovery of the valuable nitroglycerine with destruction or other use of the nitrocellulose residue, the other by the conversion of the nitroglycerine powder into a brisant blasting explosive.

Moreover, the ungelatinized smokeless powder nitrocotton containing nitroglycerine was reworked into an explosive and thus utilized economically.

The powder stocks on hand were worked over by the explosives manufacturers in one way or another, depending upon the form and composition of the powders, since they were the only ones having the facilities to do this.

RECOVERY OF NITROGLYCERINE FROM NITROGLYCERINE POWDER

Such powders as those having a high nitroglycerine content and small amounts of added materials soluble in the same solvents as nitroglycerine, such as stabilizers, gelatinizing agents like vaseline, centralites, and substituted urethanes, were primarily suited for

extraction. Also powders were extracted which on account of being in the form of thin plates, etc., were little suited for reworking into brisant explosives by grinding.

Only powders containing about 40 per cent nitroglycerine were subjected to extraction. This was done in copper apparatus constructed on the Soxhlet principle with low-boiling solvents which dissolved nitroglycerine easily but not nitrocellulose. Complete extraction required various times, depending upon the density of the powder aggregate, and the nitrocellulose was extracted down to a nitroglycerine content of 0.5 to 1 per cent.

The distilling flask was placed in a water-bath heated to the required temperature by steam. The extracted powder remaining in the receiver was finally freed from solvent by a current of steam, in order to recover the latter as completely as possible.

The Dynamit A.-G. used as the solvent dichloroethylene,¹ CHCl_2 , boiling at 55°C ., which had the advantage of being incombustible. In this way the use of combustible solvents, such as ether, with their attendant fire risk, was avoided.

The water bath must have a temperature of about 70°C . in order to maintain the solvent in vigorous ebullition. The nitroglycerine which collects in the still is finally freed by an air current at 60 to 70°C . from the remainder of the solvent which will not pass over otherwise, drawn off into hard rubber or aluminium cans and given a warm water washing in the wash house of the nitroglycerine plant, and can then be worked up into explosives just like freshly made nitroglycerine.

Charges of 300 to 400 kg. (660 to 880 pounds) of powder were extracted in this way, giving 120 to 160 kg. (264 to 352 pounds) of nitroglycerine per operation.

In view of the high cost of the volatile solvent the process naturally can only be economical when using great care in solvent recovery and reducing the unavoidable loss to a minimum.

The Westfälisch-Anhaltische Sprengstoff-A.-G. used for the same purpose the lower-boiling ether (boiling point 35°C .). A layer of water was put into the still, so that the refluxing ether containing nitroglycerine distilled off from the surface of the water and the heavier nitroglycerine sank to the bottom and was drawn off con-

¹ Obtained from the Dr. Alexander Wacker-Gesellschaft, München.

tinuously or intermittently.² This avoided a long continuing collection of hot nitroglycerine in the still.

However, since a solution of nitroglycerine in equal quantities of ether is heavier than water, the nitroglycerine collecting on the bottom may still contain considerable ether, so that an additional washing with hot water and compressed air, with consequent absorption of the ether vapors, was necessary.

According to German patent 337382 of the Westfälisch-Anhaltische Sprengstoff-A.-G. December 6, 1918, the nitroglycerine powder is partially saponified by hot, dilute acid solutions with recovery of unchanged nitrocellulose and formation of a solution of glycerine and acids. However, this method of utilization was never adopted on any considerable scale. In any case, by far the greater proportion of the powder was shot as explosives, as described below.

NITROGLYCERINE POWDER AS AN EXPLOSIVE

The horn-like aggregates of nitroglycerine powders have a lower sensitiveness to detonation the greater their size. On the other hand fine flake powder with a flake diameter of 0.5 to 1 mm., or cube powder 1 to 2 mm. on an edge, is readily detonated by a strong cap when confined in a borehole, can be packed in cartridges, and used directly as a brisant explosive in mining. Large aggregates must first be broken up.

According to German patent 337461 (1919) to the Zentralstelle für wissenschaftlich-technische Untersuchungen, Neubabelsberg, the nitroglycerine powder is first swelled by furfural in aqueous solution or emulsion and then worked up in a mixing machine with other explosive ingredients to make an explosive. According to German patent 337495 (1919) to the Köln-Rottweil A.-G., Berlin, the same method is used with the addition of mononitrocompounds. Both processes have proved difficult and disadvantageous from an explosives point of view, so that soon the various kinds of flake powder and tube powder were ground up to such a size that they could be used directly as explosives. According to German patent 332284 (1919) to the Westfälisch-Anhaltische Sprengstoff-A.-G. the powder is first softened by an aqueous solution of a volatile solvent, e.g., 50 per cent acetone solution, and then kneaded in a mixer with the

² German patent 337383 (1920) to Westfälisch-Anhaltische Sprengstoff-A.-G.

gradual addition of five to ten times its weight of water, which breaks it down to a granular paste. However, it has been found more economical and simpler to crush the nitroglycerine powder in rolls or edge runners to thin plates and then reduce this brittle form further. The product obtained then gives a lead block expansion of 330 to 350 cc., and has been used mainly in the potash mines under the name of Tri-Westfalit SN.

The plants of the Nobel Company have ground the different kinds of nitroglycerine powder in Excelsior Mills between steel discs, with an abundant flow of water, to a particle size of 0.5 to 2 mm., dried it and sold it under the name of "Energit" packed in cartridges 25 to 30 mm. diameter.

There is no difference in the action of these two kinds of powders. Brisance and apparent strength are dependent on the one hand upon the fineness, and on the other hand upon the nitroglycerine content. The gases of explosion naturally contain considerable quantities of carbon monoxide, so that their use is only possible in well ventilated places. Potash mining has consumed the largest quantities. When unconfined Energit and Tri-Westfalit do not propagate detonation, but on the other hand when well confined they attain a velocity of detonation of 3000 to 5000 meters per second. The mining authorities prescribe the use of the strongest blasting cap to ensure detonation. When well confined, fuse alone causes explosion.

On the other hand the so-called combined shooting has been found advantageous. This consists in placing one or two cartridges of black blasting powder upon the charge of Energit, the former being ignited by a fuse, and in turn detonating the latter.

In the first Mining List of February 1, 1923³ for Prussian Mining these explosives are shown among explosives for use in rock as No. 33 "Nitroglycerine Powder" with the following definition:

	per cent
Nitroglycerine.....	30-40
Nitrocellulose.....	60-70
Nitroderivatives of toluene and/ or naphthaline.....	0- 5
Paraffine and/ or urethane and/ or carbamid and/ or dicyan- diamid.....	0-10

³ Reichsanzeiger, 1923, No. 41, Appendix 2.

According to a recent decision of the Prussian Mine Safety Commission No. 33 is stricken from the Mining List and the following allowed instead and recommended to the Chief Mining Councils:⁴

No. 35. Nitroglycerine powder 1

	per cent
Nitroglycerine powder.....	94-96
50 per cent calcium nitrate solution.....	6-4

No. 36. Nitroglycerine powder 2

	per cent
Nitroglycerine powder.....	97-99
Substituted urethanes.....	3-1

After the New Regulation of Explosives in Prussia came into effect on January 1, 1924, No. 35 appeared in place of Energit and No. 36 in place of Tri-Westfalit.

The addition of the calcium nitrate solution to Nitroglycerine Powder 1 serves to desensitize it. The sensitiveness to shock and friction of the finely ground nitroglycerine powders, which can lead to premature ignitions on rough handling, are considerably reduced by the moistening by the difficultly vaporizable solution of hygroscopic calcium nitrate, and at the same time any too fine particles present are fixed. In order to prevent evaporation of the solution the cartridges are dipped in paraffine.

Transportation of these explosives is permitted as freight in unlimited quantities on German Railroads as propellants of Group 1, provided that the requirements of the propellants in question are met.⁵

SEMI-FINISHED SMOKELESS POWDER AS AN EXPLOSIVE

In the last few years the not inconsiderable supplies of smokeless powder nitrocotton containing nitroglycerine which were still on hand, have been used as explosives.

For reasons of safety in handling, a portion of the water content is left in the moist mass, and to obtain complete combustion and gases of explosion free from carbon monoxide about 25 parts of sodium nitrate or potassium perchlorate are added. The moist, flaky mass is packed by hand into cartridges which have a density of

⁴ Reichsanzeiger, 1923, No. 289.

⁵ See German Railroad Regulations, Supplement C, I, Ia, B. Propellants.

about 1, and which are dipped into paraffine to prevent evaporation of the moisture.

This explosive gives about 300 cc. expansion of the lead block, 12 mm. crushing, and provided that the moisture content does not exceed certain limits has a satisfactory sensitiveness and propagation. Detonation can only be obtained by a strong blasting cap. Combination shooting with black blasting powder and fuse is impossible, in contrast to smokeless powder explosives.

Due to the moisture content it is very difficult to ignite and burn, and very insensitive to shock and friction, so that the German Railway Administration allows it in limited freight transportation in Group 2 under the name of "Pyrolit." According to the Reichsgesetzblatt, No. 29, Part II, of August 13, 1923 the definition in question reads as follows:

"Supplement C of the Railroad Regulations is changed as follows:

"At the end of Group 2 the following new sub-group e is added: (e) Pyrolit, with appended numbers and/ or letters, Mixtures of smokeless powder raw materials with 5 to 12 per cent of its weight of gypsum and containing so much water that the finished explosive contains at least 18 per cent moisture, also with a maximum of 30 per cent sodium nitrate, which may be wholly or partly replaced by potassium perchlorate, also with a maximum of 15 per cent trinitrotoluene."⁶

The gypsum content appears because 10 per cent gypsum was added to the material to render it unfit for military purposes. The gypsum remains in them unchanged on explosion, provided that the explosive is compounded on complete combustion. With an oxygen deficiency, on the other hand, the calcium sulphate is reduced to sulphide, which reacts with the water vapor to form gases of explosion containing hydrogen sulphide.

At the time this was written the negotiations between the industry and authorities regarding the admission of the Pyrolites as mining explosives and the final decision as to composition, particularly as regards the minimum quantity of water, had not been concluded. To ensure a satisfactory propagation of detonation a reduction of the total water content to 15 per cent is desirable.⁸

⁶ The Pyrolites may until further notice be shipped in unlimited quantities as freight.

⁷ See also Reichsanzeiger 1923, No. 289. First Supplement to the List of Mining Explosives, No. 34 -Pyrolit.

⁸ In actual practice this reduction has been made.

SUPPLEMENT

CHEMICAL ANALYSIS OF EXPLOSIVES CONTAINING NITROGLYCERINE¹

QUALITATIVE TESTS

The test for and identification of nitroglycerine in guhr dynamites and explosives which contain no other important constituent which dissolves in the same solvents as nitroglycerine, is very simple.

Some finely divided guhr dynamite or pulverent dynamite is digested with anhydrous ether, filtered, and the solution allowed to evaporate on a water bath or in a warm place. The remaining oil is very readily recognized as nitroglycerine by its sensitiveness to a blow by taking up a drop of it on a piece of filter paper, placing it on an anvil and striking it with a hammer or testing it in the falling weight machine. If a drop is added to a solution of potassium iodide-starch paste acidified with sulphuric acid, and some zinc shavings added, a blue color develops.

If paraffine, sulphur or resins are present in appreciable quantities they separate after driving off the ether. The nitroglycerine is allowed to drain well, pressed several times between filter papers, and then is identified. Paraffine remains on treating with cold alcohol. Sulphur separates as crystals and may be recognized by its flame and odor on burning. Resins may be saponified by a solution of soda, and hydrochloric acid precipitates resinic acids from the soap.

The nitrogen determination in the Lunge nitrometer determines the homogeneity and purity of the nitroglycerine. If considerable quantities of aromatic nitrocompounds are present, which form with the nitroglycerine a solution or a eutectic, low-melting mixture, the blow test can fail under certain conditions. In such a case tests are made, as above, for nitric esters, or the nitric oxide evolved is measured in the nitrometer.² The nitrocompounds are identified, if possible, by crystallization from alcohol and determination of their melting points. If it is suspected that some dinitroglycerine, dinitrochlorohydrine or nitroglycol is present with the nitroglycerine, as for example in the non-freezing dynamites, the odor, volatility and solubility in water of the oily residue should be noted. If dinitroglycerine is present the oil separates on treatment with water. Dinitrochlorohydrine and nitroglycol have a somewhat peculiar odor and a characteristic volatility, which is observed on long continued heating of the oil to temperatures of 50 to 60°C.

¹ See Guttman, *Industrie der Explosivstoffe*, p. 489, 506; also Escales, *Nitroglycerin und Dynamit*, pp. 203, 255.

² Regarding the use of the nitrometer method on ether extracts see below under Quantitative Analysis.

In the case of dinitroglycerine and dinitrochlorohydrine determinations of nitrogen and chlorine will decide. Nitroglycol has about the same nitrogen content as nitroglycerine but differs in specific gravity, and can be readily distilled in vacuo at comparatively low temperatures from an oil bath. (See the corresponding chapter in Part II.)

If it is a question of a gelatine dynamite or blasting gelatine, i.e., if collodion cotton is present, the nitroglycerine can be isolated in two ways. The same thing also applies to other nitric esters. First the mass is cut by a horn spatula into small cubes or flakes, and digested with anhydrous ether, then proceeding as above. The collodion cotton remains with the dope. The other method is digestion with a little ether-alcohol (2:1), precipitation of the collodion cotton with an excess of chloroform, pressing it dry, drying and identifying by ignition, falling weight test, nitric acid reaction or nitrogen determination by the Schulze-Ticmann method. The ether-alcohol-chloroform solution is evaporated and the oil residue tested as above. Any camphor present remains dissolved in the nitroglycerine and becomes noticeable by its odor. It can be extracted by carbon disulphide.

The residue from extraction can contain kieselguhr, vegetable meals, charcoal and other coal, saltpeters, chlorates, perchlorates, chlorides and other salts, and perhaps nitrocellulose. The salts are identified by their known chemical reactions. The most common ones dissolve in cold or hot water, and from this solution the vegetable meals, coals and perhaps nitrocellulose can be filtered off. The collodion cotton is extracted by ether-alcohol, and any possible gun cotton present after removal of the collodion cotton removed by treatment with ethyl acetate or acetone. The microscopic examination of water-insoluble portions is usually sufficient to recognize the different constituents. After reducing the organic components to ash there finally remain the mineral constituents insoluble in water, such as kieselguhr, chalk, barium sulphate, magnesia, talc, caput mortuum, etc.

QUANTITATIVE ANALYSIS

Quantitative analysis is preferably preceded by a determination of moisture. Since at higher temperatures there is a certain amount of volatilization of nitroglycerine and perhaps other constituents such as aromatic nitrocompounds, the determination is best done in a desiccator. If the explosive is a loose powder it is spread out in a thin layer, if a gelatine it is cut into small pieces on a glass dish and allowed to stand in a desiccator over fresh calcium chloride until constant weight is obtained, which may require twenty-four hours or under certain conditions more. Desiccators containing sulphuric acid are not recommended on account of the danger of spilling the explosive into it. This is especially true in the case of explosives containing chlorates.

Explosives containing a normal, low moisture can be subjected to extraction directly and the determination of the moisture content made on another sample simultaneously. Unless this is done a portion of the material dried in the desiccator is weighed out for analysis.

Usually the first step in analysis in the explosives plant is extraction of the

ether-soluble constituents by anhydrous ether in a Soxhlet extractor. A stock jar of ether is kept, in which the ether stands over sticks of sodium, and when using the ether it is filtered from any floating flakes of sodium hydroxide. Since many explosive constituents dissolve slowly in ether, as for example the highly-nitrated aromatic nitrocompounds, about 5 to 10 per cent of chemically pure acetone, redistilled in the laboratory, is added to the ether, which increases the solubility of the ether for such materials.

This, however, should be avoided in the case of gelatinous nitroglycerine explosives containing nitrocellulose, because the ether containing acetone dissolves the nitrocellulose as well, which can cause a plugging of the pores

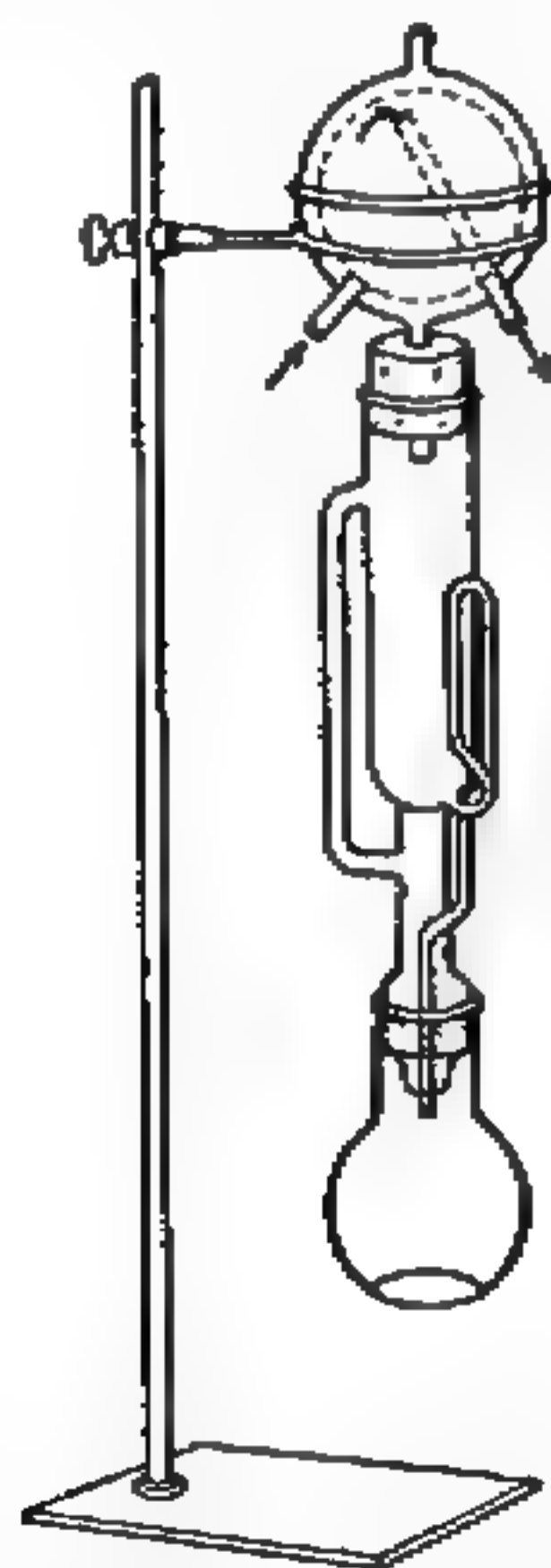


FIG. 36. SOXHLET EXTRACTOR

of the paper extraction thimble or in any case to a gelatinized extract which is inconvenient in further work. It is best to leave the nitrocellulose in the insoluble residue.

The Soxhlet apparatus consists of a distilling flask, attached tube with vapor pipe and syphon, and efficient condenser, all parts being joined by ground glass joints. Its construction is evident from fig. 36. The distilling flask rests in a moderately warm water bath, so that the ether boils quietly. A special extraction thimble² is placed in the attached tube, reaching to just below the opening of the syphon, and holding 30 to 60 grams of explosive (weighed to 0.01 gram accurately), depending upon the size of the apparatus.

² From Schleicher and Schüll, Düren.

The flask is half filled with ether, which evaporates, drops back into the thimble from the condenser, and extracts the explosive. As soon as the distillate reaches the height of the syphon tube the contents suddenly empty into the distilling flask. This operation is allowed to repeat itself until it can be assumed that the explosive is completely extracted, which usually requires four to six hours, but with blasting gelatine and gelatine dynamite longer. In the presence of substances which color ether, such as commercial nitrocompounds, complete absence of color of the ether in the upper tube indicates complete extraction.

After the ether has distilled into the upper tube and filled it, the connection is carefully broken and the ether collected in the upper tube is emptied through the syphon by inclining the former. The liquid extract is removed from the flask into a weighed dish, and the flask washed out two or three times with a little ether. The dish is allowed to stand in a warm place, at 40 to 45°C., until the odor of ether and perhaps acetone is completely gone and constant weight obtained.

If it is a question of guhr dynamite, blasting gelatine or ordinary gelatine dynamite the ether extract usually contains only nitroglycerine. The evaporation loss of the latter is very small and the result sufficiently accurate if the analysis is carefully made, contrary to the statements of Guttman.

The use of chloroform as an extracting medium is possible, but on account of its high boiling point, 63°C., and the difficult removal from the extract, it is not recommended. On the other hand, as an incombustible material, dichloroethylene, with a boiling point of 55°C., is recommended. The latter solvent mixes with nitroglycerine in all proportions and is a good solvent for aromatic nitrocompounds.

If it is suspected that dinitrochlorohydrine or nitroglycol are present, the ether is allowed to evaporate at room temperatures and then the whole warmed gently for a short time.

Nitrogen determination. The qualitative test of the extract has already been mentioned under Qualitative Tests. The possible presence of other nitric esters than nitroglycerine, such as dinitroglycerine, dinitrochlorohydrine, nitropolyglycerines and nitroglycol, can be determined by treatment with water, getting the specific gravity, or determining the chlorine and nitrogen by the nitrometer. The latter determination fails only with the nitroglycol, which is too similar to nitroglycerine (18.42 versus 18.50 per cent nitrogen, respectively). In the case of mixtures of nitroglycerine and dinitroglycerine, or nitroglycerine and dinitrochlorohydrine, as from non-freezing dynamites, a determination of the specific gravity by a pycnometer and a determination of nitrogen shows the proportions.

In making the nitrogen determination of all nitric esters extracted by ether the behavior of the extract with concentrated sulphuric acid should first be carefully tested outside the nitrometer in order to prevent accidents from too sudden a heating and reaction within the bulb of the nitrometer. To do this a few drops of the extract on a watch glass are brought into contact with some concentrated sulphuric acid and carefully digested, by a glass rod or by shaking. If there is any obvious evolution of heat it is advisable to

first weigh out the quantity to be analyzed from a pipette into a small weighing bottle cooled by ice and containing some moderately concentrated sulphuric acid, and gradually add concentrated sulphuric acid until solution is obtained. The solution can then be safely introduced into the nitrometer and the weighing bottle washed out quantitatively with small quantities of concentrated sulphuric acid.

The ether extract can contain aromatic nitrocompounds, paraffine, resins and aromatic hydrocarbons such as naphthalene, in addition to nitric esters.

Paraffine separates out as a solid. It can be pressed between filter papers and easily recognized by its external properties and melting point. If the whole extract is melted the paraffine can be separated in a separatory funnel and determined rather exactly. The resins can likewise be separated out and pressed dry. Aromatic hydrocarbons and nitrocompounds often remain wholly or partly dissolved in the nitroglycerine. If little nitroglycerine and much nitrocompound is present, attempts can be made to isolate the nitrocompound by recrystallization from a suitable solvent and identify it by its melting point, or perhaps by a nitrogen determination on the crystals.

Determination of the quantity of nitroglycerine present in a mixture of the latter with aromatic nitrocompounds by a nitrogen determination or evolution of NO in the nitrometer is possible only when it is a question of high-nitrated derivatives such as trinitrotoluene, dinitrotoluene or dinitrobenzene, which at ordinary temperatures are not nitrated further by the nitric acid split from the nitroglycerine by the sulphuric acid.

If, for example, the semi-solid or partially crystalline extract consists only of trinitrotoluene and nitroglycerine, as is the case with Donarit containing 12 per cent trinitrotoluene and 4 per cent nitroglycerine, or 3/1, a small quantity is melted in a hemispherical dish having a lip, after weighing on the analytical balance, the upper part of the nitrometer warmed by a hot, wet cloth, the quantity required for analysis dropped in, washed in with a little sulphuric acid, again weighed, and the analysis continued with certainty of accuracy. The difference is trinitrotoluene, which is not attacked by the mercury and sulphuric acid. The trinitrotoluene can be isolated from another portion of the extract by recrystallization from alcohol, and identified by its melting point, about 80°C.

On the other hand, if mononitrocompounds such as nitronaphthalene, nitrotoluene, or hydrocarbons such as naphthalene, or substituted carbamids such as centralite (from smokeless powder) are present in addition to nitroglycerine, the amount of nitroglycerine present cannot be determined by the nitrometer because the nitric acid set free by the sulphuric acid immediately acts upon the above compounds and either nitrates them or nitrates them to higher states, so that too little nitroglycerine is found.

In such a case separation is made by solvents. The extract is treated simultaneously with 65 per cent acetic acid and carbon disulphide. The former dissolves nitroglycerine fairly readily, but not the aromatic nitrocompounds, which like naphthalene are easily dissolved by the carbon disulphide, in which nitroglycerine is insoluble. The acetic acid solution is shaken several times with small quantities of carbon disulphide to extract the nitro-

compounds carried along with it, while the carbon disulphide solution is treated several times with acetic acid. The nitroglycerine is then precipitated from the acetic acid solution by water, while the nitrocompounds are obtained by evaporating the carbon disulphide.

This method gives only approximate results. Any camphor present in the nitroglycerine from blasting gelatine can also be dissolved in the carbon disulphide, but on account of its volatility it cannot be determined accurately.

The residue from the ether extraction is dried at a moderate temperature in the extraction thimble, carefully removed by pincers, and weighed. It can contain kieselguhr (in the case of guhr dynamites), nitrocellulose, wood meal or other meals, coal and mineral oils both soluble and insoluble in water. It is treated with warm, distilled water, or in case potassium perchlorate is present, a correspondingly large quantity of hot water must be used, and separated from the insoluble constituents on a weighed filter plate.⁴ The aqueous solution is made up to one liter, and in aliquot portions of the same the various components are determined either directly or after separation, by well-known methods.

The weighed, insoluble residue is shaken in a graduated cylinder with ether-alcohol or acetone to determine the collodion cotton, and after settling an aliquot portion is evaporated in a weighed dish. If it is suspected that gun cotton is present, as well as collodion cotton, the insoluble residue above is separated completely from the ether-alcohol by decantation, and the residue treated with ethyl acetate or acetone, and the gun cotton determined as under collodion cotton.

After extracting several times with solvent and decanting, the residue is finally dried and weighed, then ignited to determine the amount of organic matter by difference, and the mineral matter in the ash, insoluble in water, such as calcium carbonate, barium sulphate, iron oxide, etc., determined by well-known chemical methods.

⁴ If aluminum is present together with ammonium nitrate, e.g., in Ammonal or Ammonit 5, warm water must be avoided and the ammonium nitrate quickly dissolved by cold water and the residue filtered off, or the warm ammonium nitrate solution will oxidize the fine aluminium powder on long contact with it, form aluminium oxide, and show a higher aluminum content than was present in the original sample.—AUTHOR.

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